PRIMARY BATTERIES

H. S. CARHART

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PRIMARY BATTERIES

BY

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SIXTY-SEVEN ILLUSTRATIONS

Boston

ALLYN AND BACON

1891

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PREFACE.

WITH the exception of a single translation from the French, the material on primary batteries hitherto accessible to English readers has been in detached portions, partly in books on the general subject of electricity, and partly in scientific journals and technical papers.

A thorough knowledge, systematically arranged, of the principles involved in the construction, operation, and theory of primary batteries is of undoubted service to those beginning an extended course of study in the applications and engineering of electricity; while it is indispensable to one whose occupation requires familiarity with these most simple and useful means of producing electric currents for practical purposes.

This little book has been written with both of these classes of readers in mind. No attempt has been made to compile anything like a complete list and description of all the combinations proposed or actually used as primary batteries. A large proportion of them are more curious than useful, and many have scarcely the merit of novelty.

It is hoped that the reader will find a satisfactory account of the theory of a voltaic cell from the point of

view of the transformation and conservation of energy. In this connection the author desires to acknowledge his obligation to Dr. Lodge's "Modern Views of Electricity."

The divisions of the subject are considered to be as logical as the nature of the material permits; each one is fully illustrated by the most useful types of cells. Some prominence has been given to standards of electromotive force, since they are employed much more commonly than formerly as secondary standards for the measurement of both currents and electromotive forces. Their convenience and, with proper precautions, their accuracy as well commend them for general use.

It is hoped that the chapter on testing will be of interest to the student, and useful as an outline guide for laboratory purposes. With scarcely an exception the tests described have been made either by the author himself or under his immediate supervision. They are believed to be free from bias and to exhibit some facts not heretofore accessible to the public.

H. S. C.

UNIVERSITY OF MICHIGAN,
June 1, 1891.

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PRIMARY BATTERIES.

CHAPTER I.

ERRATA.

Page 17, line 20, for "one ten-millionth of a millimeter," read *one twenty-thousandth of a millimeter.*

Page 28, line 22, for "Edinburgh," read *London.*

Page 58, line 4, for "one of the best substitutes for nitric acid," read *nitrate of potassium and sulphuric acid.*

Page 159, bottom, for "$n \frac{E}{R}$," read $n \frac{E}{r}$.

Page 180, line 4, for "Zn, O_2, SO_4," read Zn, O_2, SO_2.

ditions, which determine that the transformed energy shall be electrical, is called a battery, or voltaic cell.

2. Batteries: Primary and Secondary. — Electric batteries may be either primary or secondary. A primary battery is usually understood to be one in which the materials are combined in the cell in such a state as to

PRIMARY BATTERIES.

CHAPTER I.

INTRODUCTION.

1. Battery Defined. — An electric battery, or cell, as a single element is called, is a device for the conversion of the potential energy of chemical separation into the energy of an electric current.

Thus the metal zinc and sulphuric acid, which acts chemically on it, represent energy of chemical separation in the potential form. If now the zinc is placed alone in the acid, this energy of chemical separation is converted simply into heat, when the zinc displaces the hydrogen of the acid with the formation of zinc sulphate. But if the displacement of hydrogen by zinc is made to take place under certain less simple conditions, then a part at least of the kinetic energy developed takes the form of the energy of an electric current. The arrangement of parts necessary to secure these conditions, which determine that the transformed energy shall be electrical, is called a battery, or voltaic cell.

2. Batteries: Primary and Secondary. — Electric batteries may be either primary or secondary. A primary battery is usually understood to be one in which the materials are combined in the cell in such a state as to

be immediately utilizable in producing an electric current; while, in a secondary battery, the materials or elements of which it is composed need to be modified by electrolysis, due to the passage of a current of electricity from some external source, before the cell is in condition to yield any considerable energy in the form of an electric current. The former possesses a store of potential energy in the materials which admit of chemical reactions; while the latter is only a reservoir, capable of storing energy by means of the chemical changes produced by electrolysis.

Some batteries may combine both characters in one. These are capable of having the chemical changes which take place in them, during the production of a current, reversed wholly or in part upon the passage of a reverse current from some other source; so that, after they have been exhausted by performing their function as a primary battery, they may again be restored to activity by the passage through them of a current in the opposite direction to the one normally furnished by the cells themselves. This reverse current must be kept flowing for a sufficient time to effect the necessary chemical changes. Such cells are not as efficient in their secondary capacity as storage cells which are designedly such. The energy which they can restore after recharging must always fall far short of the energy expended on them.

3. Origin of the Voltaic Cell. — As early as 1767 Sulzer announced to the Berlin Academy of Science the discovery that a peculiar taste is perceived when two different metals are placed together on the tongue and brought into contact at their edges. Such a combination of two metals, as copper and silver, and the saline

saliva constitutes, as we now know, a voltaic couple. But the significance of Sulzer's observation was not appreciated till more than thirty years later, when Galvani had made his capital discovery (1786) that freshly prepared frogs' legs, hung by a copper wire on an iron balcony railing, twitched convulsively whenever the frog touched the iron; and Volta had demonstrated that the effect was not due to animal electricity, but to the two metals; and that electricity, identical with that excited by friction, could be produced by means of the metals without the agency of animal tissues, nerves, or muscles. Hence arose Volta's contact theory of electrical excitation. This ascribes what is now called the difference of potential exhibited by two metals to their mere contact, independently of the medium in which they are immersed. The reader is referred to a later chapter for a discussion of this subject.

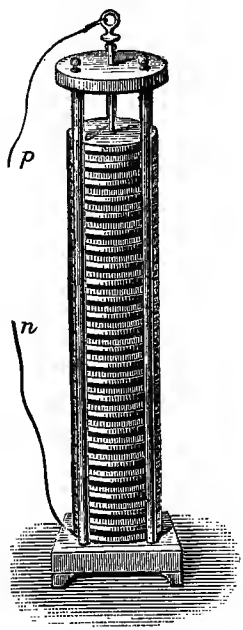


Fig. 1. — Volta's Pile.

4. Volta's Pile. — In pursuance of his view of the origin of the electricity producing the muscular contractions of the frog, and in order to increase the electrical action, Volta constructed a chain of elements, to which he gave the name of **artificial electric organ**, but which has since been known as the **Voltaic pile.** It consisted of many discs of copper and zinc, or

preferably silver and zinc, either placed in contact or soldered together in pairs, and piled up with interposed layers of cloth moistened with pure water, or better, with a solution of salt. An essential condition was that the order zinc-copper-cloth, zinc-copper-cloth, must be maintained from bottom to top. Fig. 1 shows one of the original forms of a voltaic pile. The discs were kept in position by glass rods. The bottom disc of zinc was called the **negative pole**, and the top one of copper the **positive pole**. A pile composed of from twenty to forty such pairs of plates produced appreciable physiological effects when the experimenter touched the two poles with moistened hands, or when the positive and negative terminal wires were held in the mouth or touched the eyes.

Fig. 2.
Dry Pile.

Volta's pile was the immediate forerunner of his "crown of cups," which was the first real voltaic battery. Each element of it was called a galvanic element. Thus the names of both Galvani and Volta became inseparably associated with this earliest device to produce a continuous flow of electricity.

5. The Dry Pile. — Following the principle of Volta, Behrens constructed a pile, in which the moistened cloth was replaced with paper, and which was called, in consequence, a dry pile, though it is inactive unless the paper holds more or less moisture. Zamboni, who interested himself in it and modified it, gave to it the name of Zamboni's pile. It was made of so-called gold and silver paper, the former being coated on one side with copper foil, and the latter with tin. The pairs were made of small discs of the coated paper, from $\frac{1}{2}$ to 4 cm. in

diameter, placed together with their metallic sides outward, and then piled up to the number of many hundreds in such a way that the copper of every pair was turned in the same direction. The whole column was then firmly pressed into a glass tube, varnished with shellac, and finally closed with brass caps, as shown in Fig. 2.

Dry piles were made consisting of as many as 20,000 pairs of discs. These were capable of charging a thin Leyden jar of 350 sq. cm. surface, in ten minutes, to such an extent that the discharge melted 2.5 cm. of platinum wire 0.05 mm. in diameter.

The dry pile has been applied to the construction of a device for the continuous motion of a light insulated carrier, called an electric pendulum, or perpetual motion. Two columns, S and S', Fig. 3, of about 2000 pairs each, are placed so that the positive pole of one and the negative of the other are uppermost. The lower poles are then connected metallically by a wire m, and the whole is placed on an insulating stand. The small metal ring r is attached to a glass rod forming the upper part of the pendulum, which is supported on a knife edge at a, and has a device at b for adjusting the centre of gravity, which is made to assume a position slightly above the point of support. The pendulum, therefore, inclines toward one side, receives a charge from the pole touched, is repelled, and carries its charge over to the opposite pole, by which it is neutralized, and has given to it a charge of the opposite sign. It then reverses its motion toward the pole first approached; and this action is repeated indefinitely.

Such a pendulum has been in continuous motion, it is said, in the University at Innsbruck since 1823.[1] The

[1] Müller's Lehrbuch der Physik, Vol. III. p. 249.

period of oscillation changes within limits with the humidity of the atmosphere.

The energy expended by the moving system is exceedingly small, and is at the expense of the internal chemical energy of the pile, which is necessarily limited.

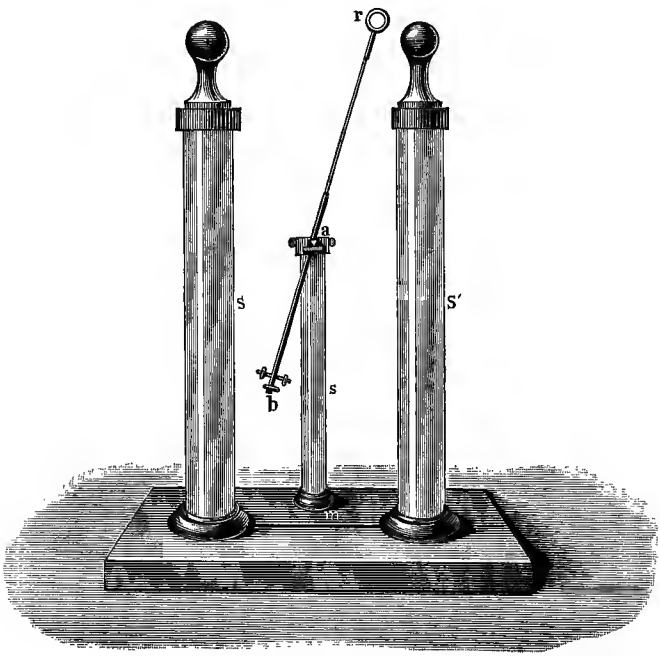


Fig. 3. — Electric Pendulum.

The dry pile has been applied in a similar way to the construction of a delicate electrometer for the detection of minute charges of electricity on a piece of gold leaf suspended between the poles; or for keeping charged the pairs of quadrants of an electrometer, similar in principle to Sir William Thomson's.

CHAPTER II.

THE SIMPLE VOLTAIC CELL.

6. Fundamental Phenomena. — If a strip of pure zinc is placed in sulphuric acid, diluted with from fifteen to twenty times its volume of water, bubbles of hydrogen may be seen to collect on the zinc, but the chemical action soon ceases. If now a strip of copper is placed in the same solution with the zinc, no change is observable so long as the two metals are kept out of contact; but as soon as they are made to touch each other, or are connected together by means of a wire or metal strip (Fig. 4), vigorous chemical action is set up, the zinc is attacked by the acid, and hydrogen gas is liberated in abundance at the **surface of the copper plate** or strip. Thus, while the chemical action takes place apparently at the zinc, the gaseous product of the reaction appears only at the copper. As soon as the connection between the two metals is interrupted, the chemical action ceases, and hydrogen is no longer disengaged.

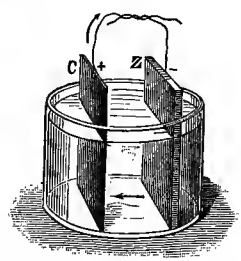


Fig. 4.
Simple Voltaic Element.

If now the proper tests are applied, it will be found that the energetic chemical activity, taking place while the two metals are connected, is accompanied by the

passage of a current of electricity from the copper to the zinc through the metallic connector, and from the zinc to the copper through the liquid in which the plates are immersed. The plates, the liquid, and the connecting wire or other conductor constitute the **electric circuit.** The wire connected with the copper plate is called the **positive electrode,** and the other the **negative.** The copper plate itself is called the **negative plate,** and the zinc the **positive plate.** This is because it has been demonstrated that zinc in contact with copper in air, either directly or through an intervening metal, assumes a positive charge of electricity, and the copper a negative one.

Such a system of two different metals, immersed in a liquid which acts chemically on one of them when the circuit is closed, constitutes what is known as a voltaic cell or element. The positive metal is usually zinc; the negative may be copper, silver, or platinum; while for the exciting liquid water, salt water, sulphuric acid, hydrochloric acid, or a caustic alkali may be used.

7. Theory of the Voltaic Element. — To make as simple a case as possible, let us suppose that the zinc and copper are immersed in dilute hydrochloric acid, every molecule of which consists of one atom of hydrogen combined with one of chlorine (HCl).

Clausius supposed that in a liquid a continual interchange takes place between like atoms of different molecules. Thus the hydrogen of any acid molecule of hydrochloric acid is not permanently attached to the chlorine of the same molecule, but is occasionally separated from it, and then combines with the free chlorine atom of some other molecule. This interchange goes on indifferently in all directions so long as no directive

force is introduced from without. The theory of Clausius is supported by certain facts of double decomposition with strongly combined salts. When their solutions are mixed, the interchange of atoms allows the formation of weaker compounds; and that such compounds do form is proved by their appearing as a precipitate, if they are sufficiently insoluble.

The chlorine and hydrogen atoms then interchange frequently from molecule to molecule at random; and while in the free state between successive pairings, each hydrogen atom carries a charge of positive electricity, and each chlorine atom an equal charge of negative.

If now we assume a chemical attraction between the zinc and the chlorine atoms, or imagine with Helmholtz that both zinc and copper have an attraction for the negative charge of the chlorine atoms, the zinc superior to the copper, then it will follow that when the zinc and copper are immersed in the liquid, an extraneous force has been introduced among the chlorine atoms, so that their molecular interchanges are constrained to take place in the direction of the zinc. They unite with the zinc, giving up their negative charge, till this action is arrested by the repulsion between the negative charge accumulated on the zinc and that of the free chlorine. Only incipient chemical action can therefore take place till electrical connection is made between the charged zinc plate and the copper immersed in the liquid with it. Negative electricity then flows toward the copper, through the connecting conductor, and unites with the positive charge of the hydrogen atoms which move toward the copper plate to meet the negative current. The hydrogen gas thus escapes at the copper plate; a procession of hydrogen atoms moves steadily in that

direction, either directly or, with greater probability, by successive molecular interchanges; and the separated electrical charges are reunited through the connecting electrical conductor. When the circuit is interrupted, the charges which quickly accumulate check the movement of the disengaged atoms by repulsion of like charges, and all chemical activity ceases.

The condition assumed when the circuit is open is one of electrostatic equilibrium. The chlorine atoms continue to unite with the zinc and to deliver to the zinc plate their negative charge, till the repulsion between the negative charges of the zinc and of the momentarily free chlorine atoms equals the chemical attraction between the zinc and chlorine. The two electrodes will then be oppositely charged, and will exhibit a difference of potential dependent upon a number of conditions to be described later.

8. Chemical Reaction in the Simple Voltaic Cell.—If we suppose that the arrangement of metals and acid in the cell is as follows,—

$$\underset{\text{Zinc}}{\text{Zn}} \;|\; \underset{\text{Sulphuric Acid}}{H_2SO_4} \;|\; \underset{\text{Sulphuric Acid}}{H_2SO_4} \;|\; \underset{\text{Copper}}{\text{Cu}},$$

then the operation which repeats itself over and over when the two metals are electrically connected may be represented thus,—

$$\text{Zn} \;|\; \overbrace{H_2SO_4 \;|\; H_2SO_4}^{\gg\longrightarrow} \;|\; \text{Cu},$$

giving

$$\underset{\text{Zinc Sulphate}}{ZnSO_4} \;|\; \underset{\text{Sulphuric Acid}}{H_2SO_4} \;|\; \underset{\text{Hydrogen}}{H_2} \;|\; \underset{\text{Copper}}{\text{Cu}}.$$

The arrow represents the direction of the current through the cell. The zinc and hydrogen are both dis-

placed in the direction of the current, while the so-called "sulphion," or SO_4 part of the acid, is displaced in the other direction. All metals and hydrogen are electropositive, and travel in an electrolyte with the positive current. Zinc sulphate is formed at the expense of zinc and sulphuric acid, and hydrogen gas is set free at the copper plate. The simple chemical action taking place is the displacement of the hydrogen of the acid by zinc, forming zinc sulphate in place of hydrogen sulphate.

9. Inconstancy of the Simple Voltaic Cell. — If the circuit, consisting of zinc, dilute acid, copper, and connecting wire, is kept closed for some time, the electric current will rapidly decrease in intensity, the chemical action will diminish, and, if the connecting wire offers but little electrical resistance, the action in the cell will shortly cease altogether. This diminution of activity is due to several causes. The chief one is the accumulation of hydrogen on the copper plate, causing what is known as the **polarization** of the cell.

The flow of the current is ascribed to what is called the electromotive force (E.M.F.), and by Ohm's law the strength of the current is the quotient of this E.M.F. and the resistance offered by the entire circuit to the flow of electricity. Any condition operating to decrease the E.M.F., to increase the resistance, or to do both, will cause the current to diminish in intensity. Now the hydrogen on the copper plate sets up an inverse E.M.F., so that the effective E.M.F., producing a current, is diminished by the value of this inverse one. Returning to the theory of the cell, it will be readily seen that both the hydrogen collected on the copper plate and the zinc will attract the free chlorine atoms.

Thus the chlorine atoms will be solicited to carry their negative charge in both directions, and the effective impulse will be the difference of the two.

The hydrogen also increases the internal resistance which the cell offers to the passage of electricity, since by its accumulation on the plate a smaller metallic surface is actually in contact with the liquid.

Independently of the hydrogen, the E.M.F. decreases because of the exhaustion of the acid and the increase in density of the zinc sulphate. Furthermore, when the zinc sulphate in solution reaches the copper plate by diffusion, some of it is liable to be decomposed by the freshly liberated or nascent hydrogen. The zinc is then deposited on the copper, the hydrogen taking its place and forming sulphuric acid. Thus —

$$H_2 + ZnSO_4 = Zn + H_2SO_4.$$

When the copper has received a coating of zinc, the two plates are electrically the same, and all action ceases. Because of these faults the simple voltaic cell is of little or no practical value.

10. Experiments on the Polarization of a Simple Cell. — Place enough mercury in a quart jar to cover the bottom, and hang near the top of the jar a piece of zinc. Fill up the jar with a nearly saturated solution of salt water, and place the exposed end of a wire, insulated with gutta percha, in the mercury, the upper end forming the positive pole of the battery. If now the circuit is closed through some simple current indicator, such as a common telegraph sounder, of a few ohms resistance, the armature will at first be drawn down strongly; but in the course of a few minutes, the time depending upon the total resistance of the circuit, the armature

will be released by the magnet, and will be drawn up by the retractile spring. Polarization has then proceeded so far that the current is insufficient to operate the instrument.

Next take a small piece of mercuric chloride ($HgCl_2$) no larger than the head of a pin, and drop it in on the surface of the mercury. It will set up a spinning movement along the mercurial surface, and the sounder armature will be at once drawn down, indicating that the current has recovered its initial value. The mer-

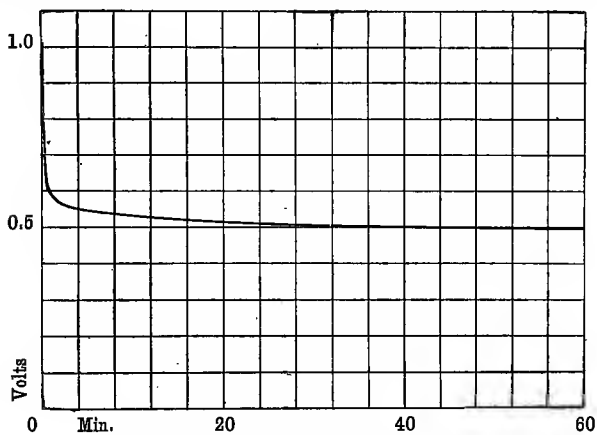


Fig. 5. — Polarization Curve of Simple Cell.

curic chloride furnishes chlorine for the removal of the hydrogen, and so reduces the polarization. In a few minutes the chloride will be exhausted, and polarization will again set in. The introduction of a little mercuric chloride will again restore the cell to activity.

A graphical representation of the progress of the polarization in a simple voltaic element is shown by the curve of Fig. 5. A plate of clean zinc and one of

clean copper were immersed in dilute sulphuric acid, specific gravity 1.05. The plates were 5 cms. apart, and 96 sq. cms. surface on each plate were under the liquid. The ordinates of the curve denote the total E.M.F. at intervals of time indicated by the abscissas. The first observations were taken at as short intervals as possible, but after the first few minutes they were less frequent, as the change in the E.M.F. was only slight. The external resistance was 20 ohms.

With a smaller external resistance the polarization curve is still steeper during the first half-minute, and in the same time the E.M.F. falls to a still lower level.

CHAPTER III.

POTENTIAL AND ELECTROMOTIVE FORCE.

11. Electric Potential. — Electric potential is defined in terms of work, and work done is the measure of the energy expended or transformed. It is sufficient for purposes of current electricity to define the **difference of potential** between two points. It is numerically equal to the work done in carrying a unit of electricity in the positive direction from one point to the other. Thus in Fig. 6 the potential difference between the terminals A, B, of the battery is the work required to transport a unit quantity of electricity from A round through the external resistance R to the point B. In general it is not the same as the work done in carrying the unit of electricity from B to A through the internal resistance r of the cell, from the negative to the positive terminal.

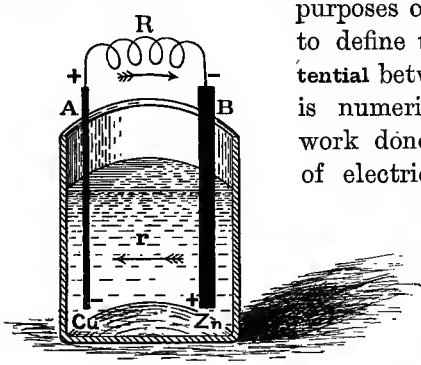


Fig. 6. — Simple Battery Circuit.

The unit employed in this definition is the "absolute" or centimetre-gramme-second (C.G.S.) unit of quantity, which is ten times the practical unit, called the **coulomb.**

A point is said to have the practical zero of potential when it is the same as that of the earth.

Since difference of potential is the work done on unit quantity, the total work done when any quantity Q is transferred from one point to the other is Q times the potential difference between the points. This remains true whether all the energy expended in the transfer is converted into heat because of the ohmic or frictional resistance R; or whether a portion is converted into mechanical work by means of an appropriate motor device inserted in the external circuit; or whether the energy is in part stored up by means of electrolysis, as in a secondary battery; or in producing a magnetic field. The work done in one second on any portion of a circuit, included between two points, is the product of the current and the potential difference, both in C.G.S. units. The work is expressed in **ergs.**

It is important to note that the portion of the circuit between the two points considered must not include any source of positive E.M.F.; that is, an E.M.F. acting in the direction of the positive current flow.

12. Positive and Negative Work. — Work done upon the current, or work done in producing a current, is to be considered positive; while work done by the current is negative. Where the work has the positive sign, energy in some other form is converted into the energy of an electric current; but when the work is negative, the energy of the electric current is in general expended in heating the circuit, in doing mechanical work, or in effecting chemical dissociation. In the voltaic element the energy of chemical separation is transformed into that of the electric current. The same is true of a secondary battery during its discharge.

In the dynamo-electric machine the power expended in driving the armature is largely reproduced in the energy of the currents traversing it.

13. Electromotive Force. — Electromotive force is the name given to the cause of an electric flow. It is now often called **electric pressure** from its superficial analogy to water pressure. The origin of the E.M.F. of a voltaic battery is in the superior affinity of zinc for oxygen as compared with copper. If equivalent weights of zinc and copper are oxidized, the heat of combustion is found to be 85,400 and 37,200 calories respectively. That is, the oxidation of 65 gms. of zinc and 63.4 gms. of copper, requiring equal weights of oxygen, will produce enough heat to raise the temperature of 85,400 and 37,200 gms. of water 1° C. respectively. The strain of the oxygen atoms toward zinc is more than twice as great as toward copper. This strain need not extend to a greater distance in a liquid than the "molecular range," which Quincke has calculated to be about one ten-millionth of a millimetre, or one five-hundred-thousandth of an inch. As fast as the oxygen is exhausted from the layer of liquid in immediate proximity to the zinc, diffusion supplies the waste. The heat of formation of equivalent weights of zinc and copper with chlorine is 97,200 and 51,600 calories respectively. With chlorides, therefore, zinc is still the positive plate, and copper the negative. If platinum is made to replace copper, the negative strain on the oxygen or chlorine atoms is reduced nearly or quite to zero, and the E.M.F. of the combination is accordingly increased.

The E.M.F. of any form of battery depends, therefore, on the materials employed, and is entirely independent of the size and shape of the plates. The condition of

the surface of the plates and the density of the solution or solutions also affect the value of the E.M.F. Thus oxidation of the copper plate increases the E.M.F., while oxidation of the zinc plate decreases it. This result is easily explained in accordance with the theory. The oxygen on the copper plate serves to remove the nascent hydrogen, thus obviating polarization. On open circuit the hydrogen is then attracted toward the copper oxide, and the oxygen toward the zinc. Both operations facilitate the electric separation and transfer of charges in opposite directions.

The view here adopted is that the effective E.M.F. of a primary battery is at the contact of the zinc and the exciting liquid rather than at the contact of zinc and copper.

14. Relation of Electromotive Force to Difference of Potential. — The two expressions are not synonymous, neither are they always interchangeable. E.M.F. establishes difference of potential rather than the reverse. This is evident from the fact that there **may** be a current without any difference of potential between successive points in a circuit, but not without an E.M.F. Such would be the case if a straight bar magnet were thrust through a perfectly uniform circle of wire along the axis of the ring. An induced current would flow along the ring during the motion of the magnet. Every part of the wire would cut equally lines of force, but all points would have precisely the same potential if measured by an electrostatic voltmeter of small capacity.

The difference of potential between two points is, however, numerically equal to the effective E.M.F. producing a current from one point to the other when the circuit between the points **contains no source of E.M.F.**

In such a case the current flows from the place of higher potential to that of lower, and the **loss** of potential is proportional to the resistance passed over. Thus in Fig. 6 (p. 15), A has a higher potential than B, and the current flows in the external circuit from the higher potential to the lower. Moreover, the difference of potential between A and B is equal to that part of the total E.M.F. of the cell which will produce the given current through the resistance R between the two points. The loss of potential in passing over different portions of this conductor is strictly proportional to the resistance of the several portions.

If, however, we direct our attention to the interior of the cell, we find that the current flows across from the zinc to the liquid, or from lower to higher potential. It is so impelled by the **vera causa** there acting to produce an electric flow. This cause, which is called an electromotive force, may be compared to a pump which lifts water against gravity; while in the remainder of the closed system of pipes, conveying the water, the liquid flows back again by gravity. It is convenient, therefore, to divide an electric circuit into two regions, one containing the source or sources of E.M.F., and the other containing none. Within the latter region the current flows from higher to lower potential, and the loss of potential is proportional to the resistance passed over. Within the other region, or at some points in that region, the current passes from lower to higher potential, and the **change** in potential bears no relation to the resistance. In all cases, however, the loss or shrinkage of potential, due to ordinary ohmic resistance, is proportional to the resistance passed over. The **change** in E.M.F. in passing over any resistance is the loss due to

this resistance, added to all the E.M.F.'s encountered, taken with their proper sign.

15. Relation of Potential Differences to External and Internal Resistance. — It will be useful to consider attentively the distribution of potential throughout the circuit of a simple cell containing no source of counter E.M.F.

If the circuit is open so that the external resistance is infinite, then the potential difference between the two electrodes is the total E.M.F. of the cell. Under these conditions the internal resistance of the cell is zero in comparison with the external resistance. Hence the total fall of potential is through the air from one terminal to the other. If now the external resistance is gradually diminished, the potential difference between the two poles of the battery becomes less and less, the E.M.F. of the battery remaining constant. If E is the total E.M.F., E' the fall of potential between the terminals of the cell, and e the loss due to the resistance of the battery itself, then

$$E' = E - e, \text{ or } E = E' + e;$$

also

$$E' : e :: R : r.$$

If now the poles of the cell are connected by a stout conductor of negligible resistance, then E' becomes zero, and e equals E. In other words, the total loss of potential is then entirely internal.

If we suppose the seat of the E.M.F. at the surface of the zinc, neglecting the negative E.M.F. at the other plate, then the zinc and connected conductors are at the lowest potential, a sudden rise occurs in passing from the zinc to the liquid, and there is a gradual fall

through the liquid to the negative plate. If the internal resistance is increased, the slope of potential per unit of resistance is diminished, but the total loss through the electrolytic conductor remains the same, and equals the E.M.F. of the cell. It is immaterial whether the two plates with the connecting conductor are partly or wholly immersed in the conducting liquid.

16. Volta's Contact Force. — The muscular convulsions which were observed when the lumbar nerves and the crural muscles of a frog were connected with a bimetallic arc of iron and copper, Galvani attributed to a separation of the two electricities at the junction of nerves and muscles. Volta showed that no effect was obtained with a continuous wire of a single metal; he therefore attributed the effect to the contact of dissimilar metals. After the invention of his pile in 1800 another theory arose, which assigned chemical action as the origin of the E.M.F. In Volta's pile the water moistening the cloth discs was said to be the exciting liquid oxidizing the zinc. Volta assigned to it the function of a conductor only. In pursuance of his theory, Volta invented a condensing electroscope with one plate of polished copper and the other of polished zinc. When the zinc plate was placed on the copper and then deftly lifted by means of an insulating handle, the gold leaves of the electroscope diverged with negative electricity.

In recent times Sir William Thomson has illustrated the Volta effect, as this has been called, with the apparatus shown diagrammatically in Fig. 7. It consists of two half-rings of zinc (Zn) and copper (Cu), placed on insulating supports in the same plane, with a narrow space between their ends. A light aluminum needle is suspended so as to turn freely round the axis of the

ring. It is adjusted to hang over one of the spaces between the zinc and copper.

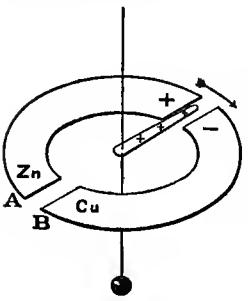


Fig. 7.
Thomson's Contact Apparatus.

If now the needle is charged to a high potential with positive electricity, it will turn toward the copper in the direction of the arrow whenever the two half-rings are metallically connected at AB. If the needle is negatively charged, it turns towards the zinc. This motion may be interpreted as meaning that the zinc is charged positively, and the copper negatively. It also means that there is a fall of potential in the air from the zinc toward the copper, for the positively charged needle moves in the direction of lower electric potential. It has been supposed by many to demonstrate that the seat of E.M.F. in a voltaic cell is at the contact of the zinc and copper.

17. Explanation of the Volta Effect. — The positive and negative charges exhibited by zinc and copper in contact in air may be explained as a simple variation from the ordinary voltaic element. They constitute an air-battery, with the plates immersed in a dielectric or non-conducting fluid; while the plates of the latter are immersed in an electrolytic conductor. But in each case the fluid bathing the plates acts chemically on both of them. The oxygen is attracted by the zinc and copper both, but unequally; and the effective E.M.F. is a differential result of the two chemical actions. Insulated zinc is at a potential of about 1.8 volts lower than the air, while insulated copper is only 0.8 volts lower,

these values being proportional to the heat of formation of ZnO and CuO. When the two metals are brought into contact, their potential becomes the same throughout; the equalization is brought about by an exchange of electricities, the zinc receiving a positive charge, and the copper a negative one. Their mean potential is then about 1.3 below the average potential of the air. But the normal difference of potential between each metal and the air in the immediate vicinity remains the same as before contact. Hence there is a slope of potential from the air next to the zinc to the air next to the copper of about one volt; and it is this slope of potential which is indicated by the movement of the needle in the Thomson instrument.

The relation of the air voltaic battery to the liquid voltaic battery may be illustrated in a different way. It will be recalled that on open circuit or with infinite external resistance, the potential difference between the zinc and copper is equal to the total E.M.F. of the battery. The copper has then a positive charge, and the zinc an equal negative one, the potential sloping from the positive to the negative. But if the metals are brought into contact, their potential is equalized, and the extreme potential difference is then between the liquid in contact with the zinc and that in contact with the copper, the former being the higher. The plates have no charge, because as fast as oxygen (or chlorine) brings negative to the zinc, and hydrogen brings positive to the copper, both charges are conveyed away by the conductor. This slope of potential in the fluid bathing the plates coexists with their uncharged state only when there is an incessant transfer of electricity throughout the entire circuit.

If now air replaces the liquid, the plates remaining in contact, and hence at the same potential, the **internal** resistance is infinite, the total E.M.F. is the difference of potential existing in the air surrounding the plates, and the plates acquire a charge, since no current is established. But since in the interior of a battery the current direction is from zinc toward copper, the slope of potential is in this same direction; therefore the zinc is positively charged, and the copper negatively.

To sum up: There are two paths between the zinc and copper plates, the external portion of the circuit and the internal. The plates are charged with electricity corresponding to the whole difference of potential of the battery only when one of these resistances or the other is infinite. When the **external** resistance is infinite, and the embracing fluid is an electrolytic conductor, the potential slopes from the copper to the zinc, from the positive charge on the copper to the negative charge on the zinc.

When the **internal** resistance is infinite (air), the plates being directly connected, the slope of potential is from the layer of air in contact with the zinc to the layer in contact with the copper through the non-electrolytic medium; while the zinc assumes a positive charge, and the copper a negative one, since in no other way can their potentials be equalized.

With two couples of zinc and copper plates in contact, one pair immersed in a conducting liquid and the other in air, the potential in both cases slopes from the zinc toward the copper through the medium; but in the former there will be a dynamic current, and in the latter only a slight electrostatic displacement sufficient to charge the plates. The displacement in the one is

continuous, in the other momentary. The seat of the electromotive force in either case is at the contact of the metals with the medium, rather than at their contact with each other. This is the more apparent from the fact that when zinc and copper in contact are placed in an atmosphere of sulphuretted hydrogen, the zinc acquires a negative charge, and the copper a positive one. In this case the chemical action on the copper is greater than on the zinc, and the electrical conditions are reversed as compared with the same metals in air. Similarly, iron and copper in sulphuric acid give a current from copper to iron through the external conductor; but in a solution of potassium sulphide the current is from iron to copper.

It is not intended to assert that there is absolutely no true contact force at the junction of two different metals. There is such a contact E.M.F. or potential difference, but it is of very small magnitude, and the evidence of its existence is very different from that furnished by the simple voltaic element. This evidence is furnished by what is known as the Peltier effect. It is a reversible heat phenomenon. The passage of a current through a homogeneous conductor produces heat irrespective of the direction of the current. But when a weak current is made to pass across a junction from copper to iron, the junction is cooled. This is due to a true contact E.M.F. which helps forward the current. Positive work is done at the junction, and energy in the form of heat is absorbed. When the current passes in the opposite direction across the junction, heat is produced additional to that depending upon ordinary ohmic resistance. The same reversible heat production may be observed at the junction of other metals and of dis-

similar substances. But in any case the contact E.M.F., which explains the reversible heat, is at most only a few hundredths of a volt; it is included in the resultant electromotive force of a voltaic element, but it is altogether insignificant in comparison with that due to chemical agency.

CHAPTER IV.

CLOSED CIRCUIT BATTERIES.

18. Distinction between Open and Closed Circuit Batteries. — It has been seen that the inconstancy of the current furnished by a battery through a fixed resistance is largely accounted for by polarization, due to the liberated hydrogen. The agent introduced into the cell to avoid polarization, either by removing the hydrogen as fast as it is formed or by preventing altogether its disengagement, is called a **depolarizer.** The distinction between open and closed circuit batteries depends chiefly upon the nature and action of this depolarizer.

A battery is entitled to be included in the closed circuit type only when it is capable of working on a closed circuit of moderate resistance for a considerable period, with but slight diminution in the intensity of the current. It is thus clearly differentiated from those cells that are adapted to stand on open circuit, without wasteful local action, and to furnish current only at intervals, and of a few seconds duration.

In a closed circuit cell the depolarizer must act with sufficient promptness and efficiency to prevent polarization quite completely, thus removing this cause of the decrease in the current.

In open circuit batteries the depolarizer may indeed be entirely absent, or it may act with so much sluggishness that it cannot prevent polarization taking place to

some extent during the action of the cell, but it destroys polarization after the circuit has been again opened. The promptness with which a cell recovers from a depression of its E.M.F. by polarization is a good criterion of the efficacy of this class of depolarizers. Batteries provided with such depolarizers occupy an intermediate position between those with a prompt acting one and those with none, of which the simple voltaic element is the type.

The more efficient depolarizers in general are liquid; the less efficient or slower acting ones, with only a few exceptions, are solid. The first class must be employed when a continuous current is required, especially if the current is of considerable magnitude. If but a small current is taken from a cell through a high resistance, then a solid depolarizer will suffice. But batteries with no depolarizer for the removal of hydrogen, or an equivalent, are adapted only to open circuit use, in which the circuit is to be closed for only a few seconds at a time.

19. The Daniell Battery. — The first constant battery was invented by Professor Daniell, of Edinburgh, in 1836. To prevent the disengagement of hydrogen at the copper plate, it is immersed in a solution of copper sulphate ($CuSO_4$). The nascent hydrogen then decomposes the $CuSO_4$, the result being the formation of sulphuric acid (H_2SO_4) and a deposit of metallic copper on the copper plate.

One form of the cell is represented in Fig. 8. *C* is a cleft cylinder of copper, and *Z* one of zinc. Between the two is a porous cup of unglazed earthenware, so that a continuous liquid circuit is maintained between the zinc and the copper. The zinc is immersed either

in dilute sulphuric acid, or better, in a weak solution of zinc sulphate; while the copper is surrounded by the solution of copper sulphate contained in the porous cup. Crystals of copper sulphate are shown surrounding the copper cylinder. These are held in a copper wire or perforated basket, and are for the purpose of keeping the solution of the copper salt saturated. The porous

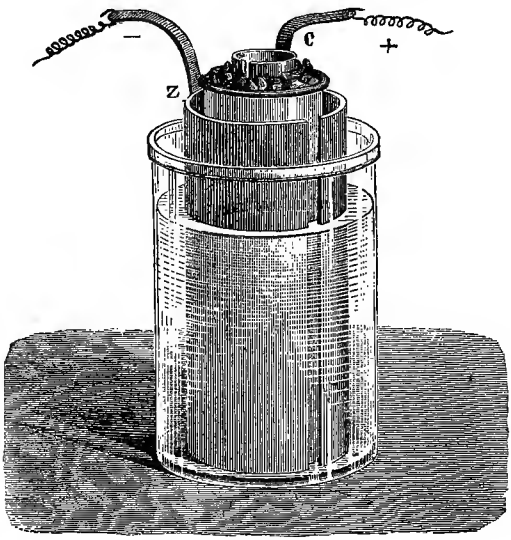
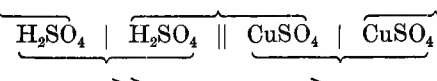


Fig. 8. — Daniell Cell.

cup serves no purpose except as a partition to separate the liquids surrounding the two plates. Each metal is placed in a salt of itself.

The more recent forms of this battery have a zinc prism and the zinc sulphate in the porous cup, while the sheet copper and the copper sulphate solution are outside. The action in either case is the same.

20. Chemical Reactions in the Daniell Cell. — With acidulated water the chemical action may be represented as follows: —

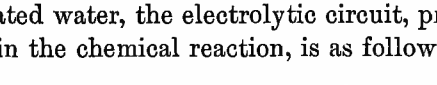


After the first step in the reaction this becomes —

$$Zn_{x-1} \mid ZnSO_4 \mid H_2SO_4 \parallel H_2SO_4 \mid CuSO_4 \mid Cu_{y+1}.$$

The arrow indicates the direction of the current, and the porous partition is represented by the double vertical line. The hydrogen and the metallic elements all migrate in the direction of the current from the zinc toward the copper plate; $ZnSO_4$ is formed at the expense of $CuSO_4$; metallic zinc disappears, and metallic copper is deposited on the copper plate. The hydrogen is intercepted by the $CuSO_4$ and never reaches the negative plate.

If the zinc is immersed in dilute zinc sulphate instead of acidulated water, the electrolytic circuit, prior to the first step in the chemical reaction, is as follows: —



After the first step: —

$$Zn_{x-1} \mid ZnSO_4 \mid ZnSO_4 \parallel ZnSO_4 \mid CuSO_4 \mid Cu_{y+1}.$$

The action taking place is a very simple one. There is, as before, a decrease of metallic zinc and an increase

of metallic copper, as indicated by the subscripts; zinc crowds copper out of the copper sulphate, so that there is a continuous transformation of $CuSO_4$ into $ZnSO_4$ by this process of replacement.

The E.M.F. of a Daniell cell, as ordinarily set up, is about 1.08 volts. The curves in Fig. 9 express the results of a test made on a Daniell cell set up with

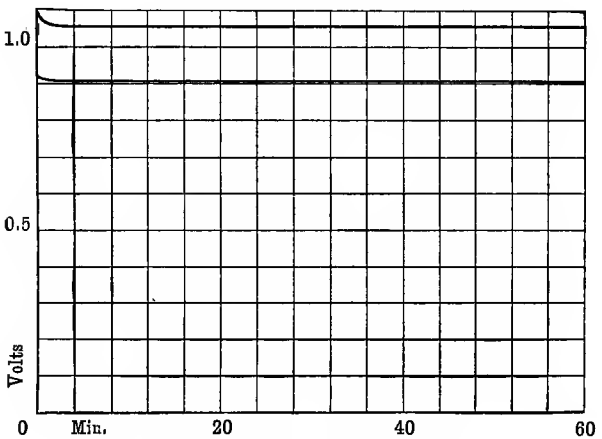


Fig. 9. — Polarization Curves of Daniell Cell.

saturated copper sulphate and a 5 per cent zinc sulphate solution. The zinc was amalgamated and the copper carefully cleaned. The external resistance was 5 ohms and the internal 0.85.

The upper curve represents the total E.M.F. at small intervals of time, which are laid off horizontally as abscissas, the E.M.F.'s being laid off on the vertical lines as ordinates. The ordinates of the lower curve denote the values of the potential differences at the terminals or electrodes of the cell for the same period of one hour.

This potential difference is the effective E.M.F. producing the current through the external resistance of 5 ohms. It is then only necessary to divide this terminal E.M.F. by five to obtain the current in amperes.

These curves should be compared with the polarization or E.M.F. curve of Fig. 5. They serve to bring out in a forcible manner the contrast between the rapid polarization in a simple voltaic element and the practical freedom from polarization of a well-constructed, clean Daniell cell. The contrast would have been still greater if the voltaic element had been tested with the same external resistance; but it was not practicable to make a satisfactory time test with an external resistance of less than 20 ohms in that case, the polarization being too rapid to follow it with accuracy.

21. Chemical Reactions of the Cell in Relation to Energy. — The question has often arisen why any chemical action should take place upon closing the circuit of a Daniell cell, set up with zinc and copper in their respective sulphates. The answer involves an explanation of the conversion of potential chemical energy into the kinetic energy of dynamic electricity, or at least a statement of the principle upon which this conversion of energy is conditioned. It depends entirely upon whether the heat of formation of the salt that can be formed by the process of replacement is greater than that of the salt or compound decomposed.

In the Daniell cell the heat of formation of equivalent weights of $ZnSO_4$ and $CuSO_4$ are 242,000 and 191,400 calories respectively. Hence for every 65 grms. of zinc entering into combination as $ZnSO_4$, with the reduction of 63.4 grms. of copper from $CuSO_4$, the difference

between 242,000 and 191,400, or 50,600, calories of heat, or the equivalent in the kinetic energy of an electric current, must be developed. In the form in which the materials are placed in the cell they represent, therefore, potential energy.

Now potential energy always tends to become kinetic whenever the conditions admit of the transformation. The sole condition in the Daniell cell is that the circuit shall be closed.

A continuous transformation then goes on, the kinetic energy appearing in the form of an electric current because of the special conditions determining the conversion; and the process continues so long as there is any available energy left to take part in the operation.

22. Local Action and Amalgamation. — Any chemical action taking place in a cell on open circuit, tending to reduce its available potential energy, or going on when the circuit is closed and not contributing to the production of the current, is called **local action.** Local action is always prominent with commercial zinc in an acid solution. The zinc contains foreign particles, such as bits of iron, carbon, or other conducting bodies; as soon as these are exposed to the liquid, they form closed local circuits, and the zinc is eaten away in patches, or pits.

To prevent this wasteful action, the zinc is **amalgamated.** Alloys of mercury with other metals are called amalgams. The process of amalgamation consists in forming a zinc-mercury alloy on the surface of the zinc plate or prism. This is best accomplished by first cleaning the zinc by immersion in sufficiently diluted sulphuric acid, and then rubbing mercury over the sur-

face by means of a swab made by tying a piece of cloth round the end of a stick. All excess of mercury should be allowed to drain off. If, however, the plates of zinc stand out of the liquid for some time, the mercury will largely separate, and collect in small globules on the surface.

Another method of amalgamating zinc is to dip it in an acid bath containing a mercury salt in solution. This may be prepared by dissolving one part of mercury in three parts by weight of aqua regia (one of nitric to three of hydrochloric acid), and then adding three parts more of hydrochloric acid.

There are other forms of local action which amalgamation does not prevent. Some of these will be more specifically described in connection with the types of batteries most unfavorably affected by them.

The zinc of a battery should always be amalgamated when the exciting liquid is acid.

23. The Effect of Amalgamation. — The action of the amalgam appears to be to bring to the surface pure zinc, while foreign materials, especially iron, are left behind. Amalgamated zinc, therefore, acts like pure zinc; foreign bodies, as soon as they are dislodged, fall to the bottom of the cell; and wasteful action, due to local currents, is avoided. But amalgamated zinc possesses the singular property of not being attacked when immersed in dilute sulphuric acid. Since this is equally true of pure and commercial zinc, the exemption of amalgamated zinc from attack is not due to the suppression of local currents. The following facts tend to show that the protection of the zinc is to be ascribed to the adhesion of a film of hydrogen to the amalgamated surface.

When amalgamated zinc is plunged in water, acidu-

lated with one-twentieth of its volume of sulphuric acid, it is not attacked at ordinary atmospheric pressure. But if a vacuum is produced above the liquid, bubbles of hydrogen are again freely evolved from the zinc surface. Upon readmission of the air, bubbles again adhere to the plate, and the chemical action is arrested.

If two plates of ordinary zinc, one amalgamated and the other not, are immersed in dilute acid, the amalgamated zinc comports itself as the zinc, and the other as the copper, of a simple voltaic couple. The amalgamated zinc is thus rather more readily attacked by the acid than the unamalgamated.

With pure electrolytic zinc and neutralized sulphate of zinc, there is no potential difference between two plates, one of which is amalgamated and the other not.

24. Relative Protection of Alloying and Amalgamating. — The investigations of Reynier show that the protection secured by mercury is much greater than is generally supposed. In certain liquids the local waste of amalgamated zinc is 50, 100, or even 10,000 times less than that of ordinary zinc.

A further question is the relative value of alloying with mercury as compared with amalgamating on the surface. Reynier concludes[1] that zinc alloyed with mercury is, in general, better than zinc amalgamated, especially in experiments of long duration.

The first superficial layer of amalgamated zinc is rich in mercury; but, as the deeper layers are attacked, the proportion of mercury diminishes, and so also the protection obtained. The opposite takes place with the alloy, which is visibly enriched in mercury as its weight

[1] Pile Electrique, p. 21.

diminishes. It is evident that on closed circuit the superiority of the alloy shows itself after a much shorter time. The alloys are more brittle than amalgamated zinc, and they become more so by use, — a fact confirming the preceding observation.

The utility of amalgamating the zinc in batteries of the Daniell type has often been contested. Experiment demonstrates that the mercury reduces the loss by one-half in a solution of 15 per cent sulphate of copper.

In the alloys referred to the mercury constituted 4 per cent of the entire mass.

In a chromic mixture, amalgamated zinc soon loses its brightness, and takes on a dark tint, while the alloy becomes brighter and brighter up to complete exhaustion.

The employment of zinc alloys contributes to the economy of batteries, and increases their constancy.

25. Defects of the Daniell Cell. — The Daniell cell has several rather serious defects. A prominent one is that the copper is sometimes deposited upon the porous cup instead of the copper plate. This deposit grows in the pores, fills them up, and finally cracks the cup and renders it useless.

Again, the diffusion of the copper salt through the porous cup, when the battery is not in action, brings it in contact with the zinc; a spontaneous displacement of copper by zinc then takes place, equivalent to local action. The copper separates in a finely divided state, and is usually oxidized and deposited on the zinc as black cupric oxide (CuO); hydrogen is at the same time given off. If the zinc becomes thoroughly blackened in this way, it should be cleaned.

Because of this local action, the Daniell battery should be taken down when not in use.

This reduction of copper and its subsequent oxidation may be illustrated by placing a piece of zinc in a dilute solution of copper sulphate. Immerse a large test-tube filled with the solution so that its open end shall be over the zinc. As it stands, gas will collect in the tube, displacing the liquid, and the solution will at length lose all its blue color. The black oxide of copper will be found in the vessel, the solution will contain zinc sulphate, and the collected gas will be found, upon testing, to be hydrogen. With dense solutions spongy copper will also be found mixed with the oxide.

Another objection to the Daniell cell for some purposes is its rather large internal resistance, considering its low E.M.F. Only a moderate current, about an ampere, can be taken from a Daniell cell as a maximum. The internal resistance will depend upon the thickness and quality of the porous cup, the size of the plates, and the distance between them. The density of the solutions affects the resistance in a minor degree.

26. The Effect of Temperature Changes on a Daniell Battery. — Professor Daniell himself found that his battery yielded a largely increased current when its temperature was raised to 100° C. He attributed this result to increased chemical activity. It is now known that the E.M.F. of this cell changes but slightly with rise of temperature, the decrease per degree Centigrade being less than 0.015 per cent.

The most important effect of a rise of temperature of the Daniell cell is the decrease in its internal resistance. It is well known that the resistance of electrolytes diminishes with increase of temperature, and that this inverse relation between resistance and temperature distinguishes electrolytic from metallic conductors, the

temperature coefficient of all metallic conductors being positive, with one exception, — an alloy of ferro-manganese and copper.[1]

Mr. W. H. Preece found[2] that when a Daniell cell was heated from 0° C. to 100° C., its resistance decreased abruptly at first, and afterwards more gradually, falling from 2.12 to 0.66 ohms. This large decrease of resistance accounts for the augmented activity observed by Daniell, the external resistance in circuit having doubtless been small.

27. The Gravity Battery. — The gravity battery is a simple modification of the Daniell, designed to avoid the use of a porous cup. It takes its name from the fact that in it the zinc and copper sulphates are separated by their difference in density. One form of this battery is shown in Fig. 10. The zinc is suspended, by means of a stout copper wire, from a brass tripod resting on the top of the jar. Thin sheets of copper, riveted together and to the conducting wire, are placed in the bottom of the cell and surrounded with crystals of copper sulphate, known commercially as "blue stone" or "blue vitriol." The zinc casting is hung in a weak solution of zinc sulphate from two and a half to three inches above the copper plates.

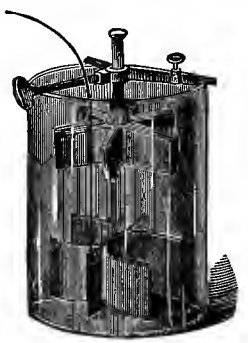


Fig. 10. — Gravity Cell.

The saturated copper salt has a density greater than the dilute zinc salt. It therefore remains in the bottom

[1] American Journal of Science, Vol. XXXIX. p. 471.

[2] Proceedings Royal Society, Vol. XXXV. 1883, p. 48.

of the jar if it is not disturbed, except that it slowly diffuses upward toward the zinc.

These cells should be set up with well-diluted zinc sulphate, extending at least an inch below the zinc. If water and crystals of copper sulphate alone are used, the cell will not work at first; and as soon as the copper salt reaches the zinc, either by diffusion or stirring, the zinc turns black from the oxidation of the reduced copper, and stalactites will soon be found hanging from the zinc.

When the cell is properly set up, with copper in copper sulphate and zinc in zinc sulphate, the chemical reactions are the same as in the Daniell cell.

If the cell is left standing on open circuit, the copper sulphate diffuses upward, as already explained, and wasteful local action takes place. Besides, the cell becomes foul much more rapidly than if the copper salt were not allowed to reach the zinc. Hence this cell always keeps in better condition if a closed circuit is maintained through a high resistance when the battery is not in use. Zinc then replaces copper in the copper salt as fast as it diffuses upward. The zinc sulphate formed must be occasionally drawn off and replaced with soft water. So, too, crystals of copper sulphate must be added from time to time to keep the solution saturated. Care must be taken not to allow these crystals to lodge on the zinc. It is better to add small quantities at frequent intervals than to place too large a supply in the jar at once.

When the water evaporates, the zinc sulphate crystallizes round the jar, and then creeps up by capillary action, crystallizing as it ascends, till it finally flows slowly over the top. As a preventive, the tops of the

jars may be dipped in hot paraffin, or a strip of very adhesive tape may be pasted round the rim, inside and out.

28. The Gethins Battery. — The inventor of this form of copper sulphate cell has sought to combine the advantages of a Daniell with those of a simple gravity cell.

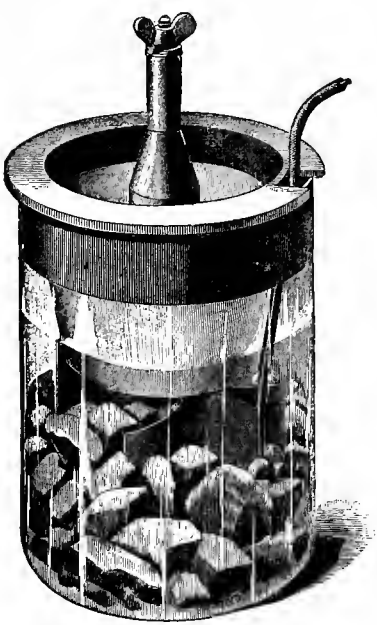


Fig. 11. — The Gethins Battery.

The cupric sulphate is placed round the sheet copper in the bottom of the jar, as in the gravity form; while a porous cup, in the shape of a frustum of a cone, is hung in the top of the jar by means of a stout rim, as shown in Fig. 11. The zinc has a broad, heavy foot, and stands in the porous cup. About four pounds of coarse crystals of $CuSO_4$ are placed in the bottom of the jar, and the jar is about half filled with water. The porous cup with the zinc is then put in position, and a weak zinc sulphate solution is poured in. The battery is then ready for use. Its E.M.F. is slightly over one volt, and its internal resistance three ohms. Hence only one-third of an ampere can be taken from it, even on short circuit; and none of this can be utilized, but all is expended in internal

heat. For energy in the external circuit, there must be external resistance in addition to the internal; and hence the current will be smaller, unless several cells are coupled in parallel.

Three of these cells in series will keep a storage battery charged so that it will run a phonograph as much as is required for a private office. The storage cell in the case tried had thirteen plates, six positive and seven negative, each 60 square inches in area. The primary battery was kept constantly connected with the secondary.

The diffusion of the zinc sulphate outward through the porous cup is noticeably greater than that of the copper sulphate inward. The level of the liquid outside the cup rises till the difference in hydrostatic pressure counterbalances the difference in diffusive tendency.

29. Delany's Modified Gravity Cell. — Cells of the Daniell type, in which copper sulphate is the depolarizer, have been of such great service when small but constant currents are required, that a brief description of the Delany modification seems desirable.

Fig. 12.
Delany's Gravity Cell.

It is shown in Fig. 12. The $CuSO_4$ is enclosed in a strawboard box, and the zinc in a paper envelope. The box prevents the $CuSO_4$ dust from dissolving at once, and diffusing so as to reach the zinc. The copper sulphate solution gradually appears by transfusion through the strawboard. The copper of the element consists of heavy wire wound in

vertical bands about the strawboard box, and an insulated wire rises from this to the top of the cell.

The paper round the zinc prevents spongy copper or other material falling upon the copper. It is claimed that no stalactites depend from the zinc, and that the deposit on the zinc is easily removed without hacking or scraping. Ordinary gravity cells often need to have this process vigorously applied to them.

A band of rubber cloth is attached by a sticky substance to the inside of the rim of the jar to prevent the crystallized salts creeping over. It is said to present a complete mechanical obstruction to the climbing of the zinc sulphate. It may, of course, be applied to any other jar, first making sure that the rim is thoroughly clean; then after warming the sticky side of the cloth, press firmly all round against the rim.

30. Sir William Thomson's Tray Battery. — Another form of Daniell cell was designed by Sir William Thomson, with a view of diminishing the internal resistance. The cell is made in the form of a large wooden tray, about 20 inches square, lined with lead on which copper has been deposited by electrolysis or during the action of the battery. The lead extends over the outside at the four corners and down under the bottom, for the purpose of making contact with the next cell below.

The zinc is in the shape of a grate, as shown in Fig. 13, which represents five cells in series. At the corners are feet turned upward. The lead of the cell above rests on the upturned feet of the zinc, making a good electrical connection on account of the weight of the cell.

Copper sulphate crystals are spread evenly over the

bottom of the tray, and the zinc is made to rest on four blocks of paraffined wood at the corners. A parchment diaphragm is sometimes placed above the copper sulphate, and a dilute solution of zinc sulphate, density 1.10, is poured on this till it covers the zinc.

These cells or trays may be piled up to the extent of ten. The internal resistance may be as low as 0.2 ohm. The circuit must be kept closed to prevent copper sulphate reaching the zinc. To secure a fairly constant current, the density of the zinc sulphate must not be allowed to greatly exceed 1.1. Some of the liquid at the

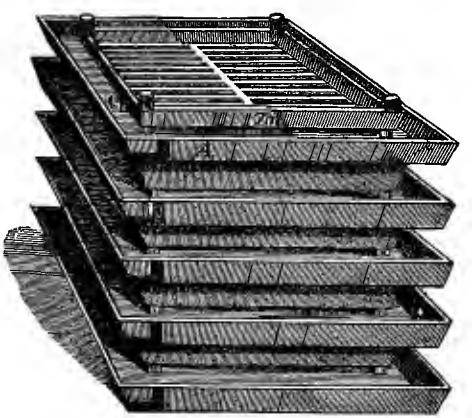


Fig. 13. — Sir William Thomson's Tray Battery.

top must be withdrawn daily, and soft water must be added in its place.

Sir William Thomson's cell was originally designed to work the siphon recorder in submarine telegraphy.

31. Grove's Battery. — The Grove battery consists of a cleft cylinder of zinc immersed in dilute sulphuric acid (1 : 12), and a thin plate of platinum in strong

nitric acid (HNO_3) contained in a porous cup. The nitric acid is a powerful oxidizing agent; and, in consequence of this property, it acts as an efficient depolarizer by oxidizing the hydrogen. The nitric acid is easily decomposed, and the nascent hydrogen readily abstracts oxygen from it. The electric chain may then be represented as follows: —

$$\overbrace{Zn_x \mid \underbrace{H_2SO_4}} \mid \overbrace{\underbrace{H_2SO_4} \parallel 2\underbrace{HNO_3}} \mid \underbrace{HNO_3} \mid Pt.$$

After the first step in the chemical reaction this becomes —

$$Zn_{x-1} \mid ZnSO_4 \mid H_2SO_4 \parallel 2HNO_3 \mid HNO_2 \mid H_2O \mid Pt.$$

On one side zinc sulphate is formed as usual at the expense of zinc and sulphuric acid; while on the other a molecule of nitric acid loses one atom of oxygen, becoming nitrous acid (HNO_2). As the action proceeds, the nitrous acid may lose another atom of oxygen, hyponitrous acid (HNO) remaining. Or further, the nitric acid may break up entirely, according to the following reaction: —

$$3H + HNO_3 = 2H_2O + NO.$$

The products are water and nitric oxide. This last is a gas which takes up more oxygen on escaping into the air, forming the red fuming nitrogen peroxide, NO_2. These fumes are highly corrosive, and are the most objectionable feature of the Grove cell. When a large current is taken from a Grove battery, the nitric acid has the appearance of boiling, on account of the rapid disengagement of the nitric oxide. The acid is carried

off as a spray, corroding the metallic connections and vitiating the air. This battery should therefore be placed in the open air or in a strong draught, and the connectors should be frequently examined and cleaned.

The zinc cylinders must be kept well amalgamated, and the platinum plates should be heated to redness occasionally to prevent their becoming brittle from some unexplained cause. These cells must be taken apart and washed with an abundance of water every time they are used.

They have the advantages of high E.M.F. and low internal resistance. The former is from 1.8 to 1.9 volts, and the latter is about 0.15 ohm, with a cell 20 cm. high and 9 cm. in diameter. Such a cell is therefore capable of giving 12 amperes on short circuit, or through an external circuit of no appreciable resistance.

Before the introduction of dynamo-electric machines and the storage battery, forty Grove cells, requiring only seven or eight pounds of nitric acid, served the writer for many years whenever a brilliant arc light was needed or projection experiments in spectrum analysis were performed.

When the nitric acid becomes dilute by the process of decomposition in the porous cup, the reaction may be quite different from that represented above. The acid may give up its oxygen entirely, with formation of nitrate of ammonium. The action may be represented by the following chemical equation: —

$$2\,HNO_3 + 4\,H_2 = 3\,H_2O + NH_4NO_3.$$

The presence of the salt of ammonia in an exhausted Grove cell can be demonstrated by testing the liquid in the porous cup for ammonia in the usual way, by heating

with powdered lime and water. A saturated solution of ferric chloride, to which 4 per cent of nitric acid has been added, has been recommended as an excellent substitute for nitric acid in a Grove cell. The E.M.F. is then intermediate between that of a Grove and that of a Daniell.

32. Bunsen's Battery. — Soon after the invention of the Grove battery, Bunsen modified it by substituting

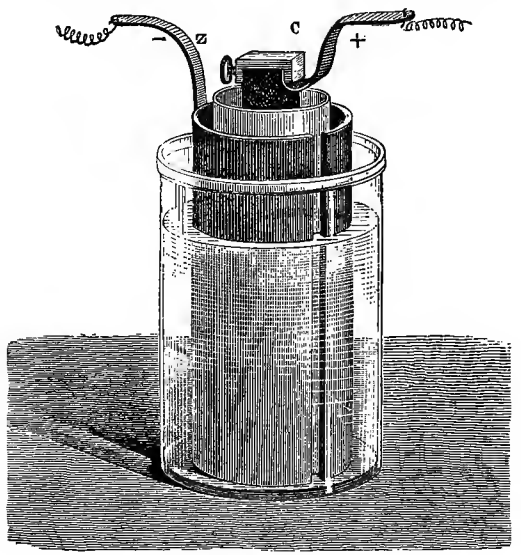


Fig. 14. — Bunsen Cell.

a prism of baked carbon for the platinum. This is an advantage in point of economy. The E.M.F. is slightly less than that of the Grove. The usual construction of the Bunsen cell is shown in Fig. 14.

The chemical action in the Bunsen battery is precisely the same as in the Grove. The hydrogen is

intercepted by the nitric acid, and is thus prevented from reaching the carbon prism by oxidation.

Another modification of the Grove cell consists in substituting an iron plate for the platinum in strong nitric acid. On account of the passivity of iron in concentrated nitric acid, it does not dissolve; and it is strongly electro-negative. When the acid becomes weak, however, by the decomposition due to nascent hydrogen, the acid attacks the iron with disengagement of corrosive fumes. On this account iron is not used in practice for the negative plate.

33. The Bichromate Battery. — If the bichromate of potassium or of sodium in solution is treated with sulphuric acid, chromic acid is formed. This compound (CrO_3) is not only rich in oxygen, but it gives it up readily to nascent hydrogen. Hence the application of bichromates as depolarizers.

An ordinary Bunsen cell may be set up as a bichromate cell by placing the amalgamated zinc cylinder in dilute sulphuric acid as usual, and filling the porous cup, holding the carbon prism, with a solution of the bichromate salt acidulated with sulphuric acid. Or, since both solutions contain sulphuric acid, the porous cup may be dispensed with entirely, both the zinc and the carbon being immersed together in the strongly acidulated bichromate solution. In this case the zinc is usually placed between two flat plates of carbon, an arrangement adopted simply to reduce the internal resistance of the cell. The E.M.F. does not differ materially from that of the Bunsen.

Fig. 15 represents one of the forms of this cell which has been much used, though it is not to be recommended. The zinc is attached to a rod, *a*, by means of

Fig. 15.
Bichromate Cell.

which it can be drawn up out of the liquid when the battery is not in use. The carbon plates are fastened to a metallic clamp, which is attached to the hard rubber top of the cell. The top of the zinc is covered with an insulating strip to prevent direct contact with the carbons.

Many forms of "plunge" battery for bichromate solutions have been devised. These are usually arranged as a battery of four or more cells, with the zincs and carbons suspended from a frame, by means of which they may all be lifted out of the liquid together by a windlass. Such a battery is shown in Fig. 16. It is a very

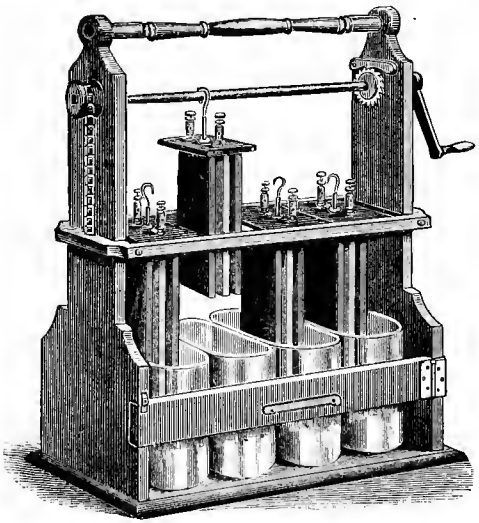


Fig. 16. — Plunge Battery.

convenient form for experimental work in physical demonstrations.

If the current falls off because of the exhaustion of the liquid in contact with the plates, it may be increased again by lifting the plates, by stirring the liquid, or by blowing air through, as is done in the Byrne battery.

One inventor gives a slow motion to the carbon plates by means of a small electric motor. Gendron has recently described a bichromate cell, in which the zincs can be easily replaced without interrupting the current. By a system of automatic valves the exhausted liquid is withdrawn at the bottom, while a constant level is maintained by the supply.

The initial E.M.F. of a bichromate battery is a little in excess of two volts per cell.

34. Chemical Reactions in the Bichromate Battery. — When a solution of bichromate of sodium or of potassium is treated with sulphuric acid, a purely chemical reaction takes place, resulting in the formation of chromic acid. Thus: —

$$Na_2Cr_2O_7 + H_2SO_4 = Na_2SO_4 + H_2O + 2\,CrO_3.$$

The chromic acid, CrO_3, is the useful agent to effect depolarization by the oxidation of hydrogen. The process is supposed to be represented by the following reaction: —

$$6\,H + 2\,CrO_3 + 3\,H_2SO_4 = 6\,H_2O + Cr_2(SO_4)_3.$$

The final result is, therefore, the production of the sulphate of zinc (at the positive plate), the sulphates of sodium and chromium, and water. It will be observed that, while all the oxygen atoms of a bichromate of sodium molecule unite with hydrogen to form water, only three of the seven are concerned with the removal

of the hydrogen displaced by the zinc. The other four oxygen atoms unite with the hydrogen coming from the four molecules of sulphuric acid, which take part in the reactions written above. Only three-sevenths of the oxygen contained in the bichromate salt, therefore, are useful in removing the polarizing hydrogen; and for every three parts of sulphuric acid which are supplied to act on the zinc, four more must be added to decompose the bichromate and to release oxygen.

When potassium bichromate is used, a double sulphate of potassium and chromium, $K_2Cr_2(SO_4)_4$, crystallizes out of the liquid as soon as it becomes saturated with these salts. This is known as chrome alum. The crystals attach themselves in a compact mass to the bottom of the jar, and are difficult of removal.

35. The Advantages of Sodium Bichromate over Potassium Bichromate. — The advantages arising from the use of the sodium salt in place of the corresponding one of potassium, appear not to have been appreciated till quite recently. But the sodium salt is to be preferred for the following reasons: —

First. It contains a larger percentage of available oxygen. The molecular weight of sodium bichromate is 262.4, and of potassium bichromate 294.6. The two molecules contain the same weight of oxygen. For equal depolarizing capacity, therefore, about 11 per cent less of the sodium salt is required than of the potassium. Unless the cost of the sodium salt is more than 10 per cent higher than that of the potassium salt, the former is the cheaper.

Second. It is much more soluble. The potassium bichromate must be dissolved by the aid of heat, and not more than about 100 gms. to the litre will remain in

solution when the liquid cools. The sodium salt dissolves in the cold, and in any quantity desired. A denser solution can therefore be used with two distinct advantages in this respect alone. The first one very evidently is that the battery does not need to be replenished with fresh solutions so frequently. The other advantage is not so obvious, but it becomes apparent when attention is drawn to the fact that there is no liberation of gas in this battery to stir up the liquid; and the exhausted solution in contact with the carbon plates is replaced by fresh portions only by diffusion, unless the liquid is agitated by lifting the plates or by other mechanical means. The denser sodium bichromate solution is not so soon exhausted of useful oxygen, and will therefore maintain a large current with a smaller rate of enfeeblement.

Third. The double sulphates of sodium and chromium, if indeed they are formed at all, do not crystallize out as in the case of the potassium chrome alum, but remain in solution. The cells are therefore easily cleaned.

36. Directions for Setting up a Bichromate Battery. — For the solution, Bunsen recommends the following proportions: —

Bichromate of potassium . . .	77.5 gms.
Sulphuric acid	78.5 c.c.
Water	750. c.c.

The bichromate must first be dissolved by heating the water to boiling. Time will be saved by crushing the crystals in a mortar before putting them into the water. After the solution has cooled, the acid may be slowly added. The acid should be poured into the water, and

not the water into the acid. After cooling again, the solution is ready for use.

Reference to the chemical action of this battery shows that for every molecule of $K_2Cr_2O_7$ used, seven molecules of H_2SO_4 are needed, provided the depolarizer is entirely exhausted of its oxygen. The molecular weight of $K_2Cr_2O_7$ is 294.6, and the seven molecules of H_2SO_4 weigh 686. Hence, to find the weight of actual acid, corresponding to 100 gms. of the bichromate, write the proportion —

$$100 : x : : 294.6 : 686.$$

Whence $$x = 232.8.$$

But sulphuric acid of density 1.8 contains 86 per cent of acid. Hence about 271 gms. of 86 per cent acid are required to furnish the 232.8 gms. of actual acid. This is equivalent to 150 c.c., density 1.8.

But since the salt in solution cannot all be utilized to effect depolarization, a residue always being left in the spent liquor, the amount of acid may be reduced. It is better to add a small quantity of fresh acid occasionally rather than to supply too much at first.

If sodium bichromate is used, 200 gms. may be dissolved in a litre of water, and to this should be added 150 c.c. strong acid. When the battery begins to show signs of exhaustion, an additional 25 to 50 c.c. per litre may be added. For complete exhaustion of the oxygen from 200 gms. of sodium bichromate, about 600 gms. of 86 per cent acid would be required. This includes the quantity necessary to form the chromic acid, and to act on the corresponding weight of zinc.

If the sodium salt is powdered, it may be put into the water, and the acid added to the solution at once. Com-

plete solution will quickly take place, and the mixture is ready for use as soon as it cools.

37. The Fuller Bichromate Cell. — The special object in the design of the Fuller battery is the continuous amalgamation of the zinc. It is shown in section in Fig. 17. The zinc, to which a brass rod covered with gutta percha is attached, is placed in a porous cup, and an ounce (30 gms.) of mercury is poured in. The cup is then filled with water, and is placed in the glass or earthen jar containing the solution of bichromate and acid and the carbon plate. The acid diffuses through the porous cup fast enough to act continuously on the zinc, which has enough mercury surrounding it to keep it well amalgamated. This insures minimum local action and constancy of current, especially if the current is small.

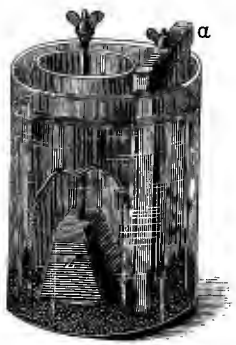


Fig. 17. — The Fuller Bichromate Battery.

Many thousands of these cells have been in use in the Post-office installation in London, and have given good satisfaction. Each cell is said to serve an entire year by replenishing with acid ten times and potassium bichromate five times. At the end of a year the battery is dismounted, cleaned, and furnished with new zincs.

38. Chromic Acid as the Depolarizer. — Instead of employing either of the preceding bichromates for the supply of chromic acid, the acid may be used directly. It may be obtained in the form of a powder, and is soluble in the acidulated water.

Since one molecule of a bichromate furnishes two of

chromic acid, it will readily be seen that ten-thirteenths as much powdered chromic acid is required as sodium bichromate. The amount of sulphuric acid is only slightly less. Experiment shows that 150 gms. per litre make a very serviceable solution. The initial E.M.F. is then 2 volts.

Another modification, known as the Ward and Sloane battery, employs zinc in caustic soda and carbon in a mixture of chromic acid, nitric acid, and common salt. The proportions are as follows: To one-half gallon of nitric acid add one and a half pounds of chromic acid and one pound of salt. This will make one charge for the porous cup of a cell $12 \times 12 \times 9$ inches. The zincs are the equivalent of twenty-four rods half an inch in diameter, and the carbons are equivalent to fifty electric-light carbons. The initial E.M.F. is 2.9 volts. Such a cell has an internal resistance of one-tenth ohm, and will give a current of 10 amperes for 30 hours; final E.M.F., 2.3 volts.

The following solution has been found by Mr. J. W. Swan (British Association, 1889) to give the best results: —

Nitric acid (density 1.42) . .	1 part	by weight.
Chromic acid	3 parts	"
Sulphuric acid	6 "	"
Water	5 "	"

The chromic acid is first dissolved in the water; the nitric acid is then added, and finally the sulphuric.

This solution requires ten parts of acid to five of water. It is scarcely possible to avoid wasteful local action with even well-amalgamated zinc in such a concentrated acid solution.

The suggestion has recently been made to use with bichromates only enough sulphuric acid to decompose the salts and release chromic acid, and then to add at least as much hydrochloric acid as sulphuric. It is claimed that there is less liability of crystallization and less heat with increased steadiness of current.

39. The Partz Acid Gravity Battery. — This zinc-carbon element possesses several points of novelty and exhibits excellent qualities under appropriate tests. It is, in fact, the application of the gravity principle to an acid depolarizer. For this purpose a flat carbon plate, with surface increased by means of pointed cones, corrugations, or holes, lies in the bottom of the cell; and a carbon rod, with the proper taper at the lower end to fit tightly into a hole in the plate made to receive it, leads to the positive terminal on top of the cell. The zinc is either a heavy cylinder where a porous cup is employed (Fig. 18), or a large horizontal plate in the form without porous cup (Fig. 19). In the former case the cup is paraffined to a height of two inches from the bottom to prevent entrance of the acid depolarizer.

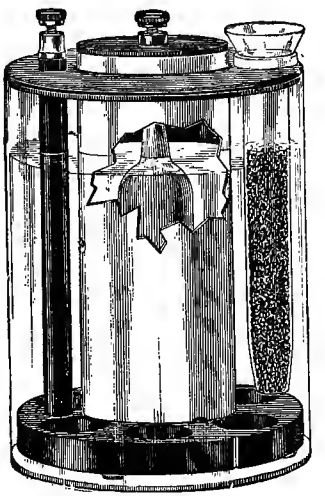


Fig. 18.
Partz Acid Gravity Battery.

The depolarizer is a sulpho-chromic salt, in which sulphuric acid has been caused to unite with chromic acid in an amorpho-crystalline state. It is supplied to

the cell when everything else is in place, by filling into the vertical tube shown in the cut to the level of the liquid in the cell. The salt slowly dissolves and diffuses over the bottom so as to cover the carbon plate.

The excitant is either sulphate of magnesium or common salt. The internal resistance is somewhat lower with the latter.

Whenever the cell shows a tendency to weaken and fail, it is necessary only to add one or two tablespoon-

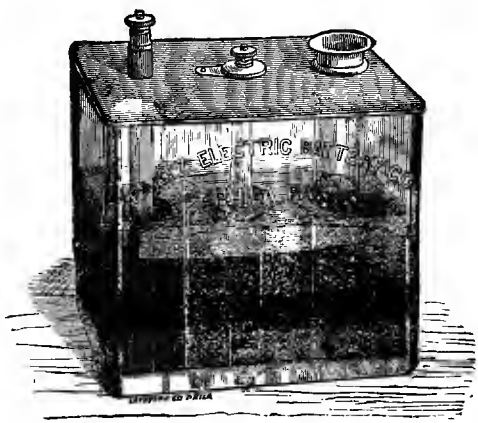


Fig. 19. — Partz Acid Gravity Battery.

fuls of the sulpho-chromic salt through the tube to restore the current to its normal value. After the spent salts have accumulated to such an extent as to interfere with the working of the cell, it is better to turn out the contents, soak the carbons in warm water, amalgamate the zincs, and set up again with fresh solutions.

Since the depolarizer is intended to remain in the bottom of the cell, it is apparent that this battery must be left as much as possible undisturbed.

The form of Fig. 19 is set up by dissolving 11 oz. of magnesium sulphate in the required amount of water and filling the vertical glass tube to the level of the liquid with the sulpho-chromic salt. One of these cells was tested for E.M.F., internal resistance, current, and polarization. The initial E.M.F. was 2.08 volts; and in the course of an hour on a closed circuit through one ohm external resistance it fell to 1.85 volts, but recovered to 2 volts again in a few minutes after opening the circuit. The internal resistance was 0.82 of an ohm, and the current about 1.04 of an ampere.

40. Taylor's Battery. — This is a zinc-carbon element capable of maintaining a very large current with small diminution of E.M.F. The carbon rods, eight in number, are attached to a well-shellacked wood cap (Fig. 20) and make contact with the brass plate shown on top. The zinc plate has an active surface of 27.5 square inches, is thoroughly amalgamated, and is wholly immersed in the dilute sulphuric acid (1 : 15). Contact is made with the zinc plate by means of a heavily amalgamated copper wire, shown in the cut. As the E.M.F. between amalgamated zinc and amalgamated copper is very small, the loss from this cause is inappreciable.

Fig. 20.
Taylor's Battery.

On account of the thorough amalgamation of the zinc, the loss due to local action on open circuit is small.

The initial E.M.F. is 1.9 volts, the current on short circuit 10 amperes, and the internal resistance as low as

0.18 ohms. The cell shown weighs, charged, 10.5 lbs. (4765 gms.), and has a capacity, it is claimed, of 70 ampere-hours.

The depolarizing solution is one of the best substitutes for nitric acid, and is rich in oxygen.

41. The Copper Oxide Battery. — It has been remarked that, in general, the best depolarizers are liquid. There are, however, two exceptions which exhibit notable efficiency. They are the oxide of copper and the chloride of silver. Both of these solids readily give up their non-metallic element to nascent hydrogen, and by reduction to the metallic state become excellent conductors.

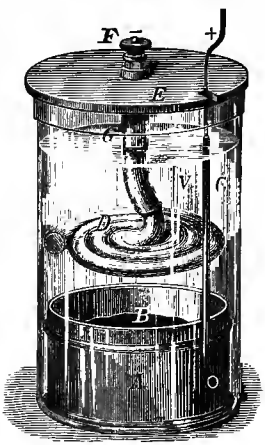


Fig. 21.
Copper Oxide Battery.

The copper oxide cell appears to have been introduced by Lalande and Chaperon, and one of the forms was that shown in Fig. 21. The spiral of zinc is immersed in a solution of caustic potash or caustic soda, 30 or 40 parts to 100 of water. The upper vertical part of the zinc *G*, where it passes out of the solution, is covered with a caoutchouc tube to prevent local action at that point. The negative consists of a cup of sheet iron containing the copper oxide *B*. To this cup is riveted an insulated copper wire which passes up through the cover and forms the positive electrode. To prevent action upon the alkaline solution by the carbonic acid gas of the air, it is covered with a thin layer of heavy petroleum oil. The height of the glass jar is 15.5 cm., and the diameter 10.5.

The larger pattern of cell is that of Fig. 22. Here the zinc is a helix of rolled metal suspended from an ebonite cover, which is held in place by means of flanges and nuts. The cell is capable of furnishing 12 amperes, and has a capacity of 540 ampere-hours.

The copper oxide battery, invented by Lalande and Chaperon, has a capacity for work per unit weight greater than any other, either primary or secondary. One kilogramme (2.2 lbs.) is able to furnish 255×10^{10} ergs, or 188,060 foot-pounds. A disadvantage is that only a part of the iron surface, constituting the negative plate, is provided with the cupric oxide sufficiently near to be of any service in the removal of the hydrogen, which accumulates on all portions of the inner metallic surface. The reduced copper, too, is not in good contact with the surface of the iron cell. The conversion of the alkali into a carbonate, by absorption of carbon dioxide from the air, necessitates the closing of the cell against admission of the air, or else the use of the heavy petroleum oil. The larger cell is closed, and has a relief valve of rubber tubing.

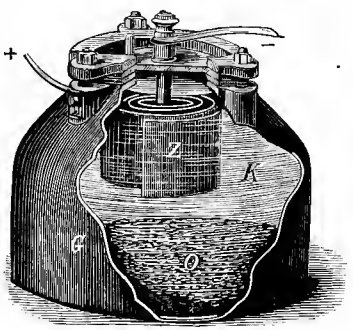


Fig. 22. — Copper Oxide Battery.

The chemical reaction taking place may be written in the form already employed in several cases.

Before the first step —

$$\overbrace{Zn_x \mid 2NaOH}^{\gg\longrightarrow} \mid \underbrace{2NaOH}_{\gg\longrightarrow} \mid \overbrace{CuO}^{\gg\longrightarrow} \mid \overbrace{CuO}^{\gg\longrightarrow} \mid Fe.$$

After the first step, this becomes —

$$Zn_{x-1} \mid Na_2ZnO_2 \mid 2\,NaOH \mid H_2O \mid CuO \mid Fe—Cu.$$

Zinc displaces hydrogen from the caustic alkali, forming sodium (or potassium) zincate; while the ejected hydrogen, travelling with the current, arrives at the cupric oxide, from which it abstracts oxygen, and metallic copper is thus reduced at or near the iron of the cell.

42. The Edison-Lalande Battery. — Recognizing the good qualities of the copper oxide as a depolarizer, Edison has devised a form designed to meet the objections noted above. The copper oxide is employed in the form of a compressed slab, which, with its connecting copper support, serves also as the negative plate.

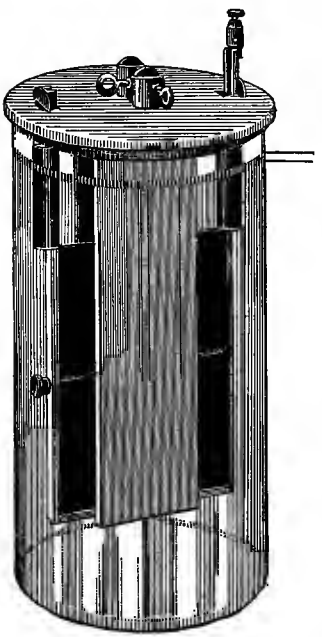


Fig. 23. — Edison-Lalande Battery.

Two of these plates are enclosed in a copper frame, on the longer arm of which is the binding post. A hard rubber safety plug in the middle prevents the zinc plate on either side from making contact with the copper oxide and copper supporting frame. One, two, or three of these copper oxide plates are used, according to the size and capacity of the cells. The weight of the oxide plate for a 15 ampere-hour cell is 2 oz., and for a 300 ampere-hour cell 2 lbs.

Fig. 23 is a 300 ampere-hour cell complete. The cover is porcelain, with small openings for the zinc and copper terminals. Since this cover does not exclude the air, the formation of a carbonate is prevented by pouring on top of the solution of caustic potash (KOH) a small quantity of heavy paraffin oil, so as to form a layer about one-fourth of an inch deep. It is of vital importance that this oil should not be omitted. If it is not used, the life of the cell is reduced fully two-thirds.

If the cell is required to furnish a strong current at once, it should be short-circuited for ten or fifteen minutes the first time it is used. By this means enough metallic copper is reduced to form a good conducting surface, and the internal resistance of the cell falls to its normal working value. Subsequent short-circuiting should, of course, be avoided, especially because the internal resistance is very low, and the large current flowing causes a great waste of material in the cell. In recent cells the device has been resorted to of reducing a superficial film of copper on the oxide before it is sent from the factory.

The 300 ampere-hour cell shown is $11\frac{1}{4}$ inches high and $5\frac{3}{8}$ inches in diameter. Its internal resistance is about 0.03 ohm, and its working E.M.F. about 0.7 volt. It is capable of delivering 14 amperes. On open circuit there is practically no local action.

The zinc should be well amalgamated.

Pressed copper oxide plates have also been used abroad in a cell having the form of Fig. 24, in which the compressed plates, *B*, are held in contact with the sheet iron, *A*, by rubber bands. The cell is closed to prevent entrance of air, but has a relief valve, *H*, for

the escape of accumulated gas. The small zinc surface, V, means relatively large internal resistance. The plates are made by mixing copper oxide with from 5 to 10 per cent of magnesium chloride, and heating the thick mass in an iron mould.

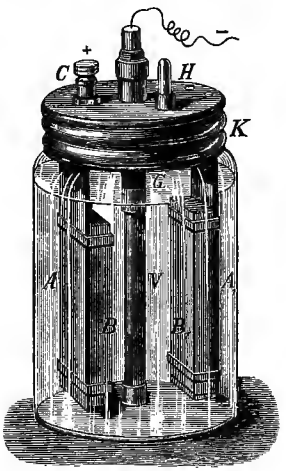


Fig. 24. — Battery with Compressed Plates of CuO.

43. The Chloride of Silver Cell. — Marié Davy appears to have been the first to suggest the use of silver chloride as a depolarizer about 1860; but it was brought into prominence by the investigations of Warren de la Rue, who constructed a battery of this kind containing 15,000 cells.

The elements are zinc and silver, and on the silver is cast the silver chloride, which is readily reduced to metallic silver by nascent hydrogen. The chloride of silver is easily melted in a porcelain crucible, and may be cast on a silver wire in a hard carbon mould. Silver foil has sometimes been cast in the chloride to give better conductivity. The exciting fluid of De la Rue's battery is ammonium chloride, and contains 23 gms. to one litre of distilled water. A denser solution dissolves silver chloride. The silver and its chloride are surrounded with a small cylinder of vegetable parchment paper (Fig. 25), to prevent short circuits internally, and the zinc rod and silver wire are held in a paraffin stopper. The silver wire of one cell is wedged into the zinc rod of the next.

The following chemical action takes place: —

$$\overbrace{Zn_x \mid \underbrace{2\,NH_4Cl}} \mid \overbrace{\underbrace{2\,NH_4Cl} \mid \underbrace{2\,AgCl}} \mid Ag_y =$$

$$Zn_{x-1} \mid ZnCl_2 \mid 2\,NH_4Cl \mid 2\,NH_4Cl \mid Ag_{y+2}.$$

This may be considered the normal action; but where the cell is worked hard, it may happen that the ammonic chloride loses chlorine faster than it recovers it from the silver chloride; and the ammonium breaks up into ammonia and hydrogen. The ammonic hydrate thus

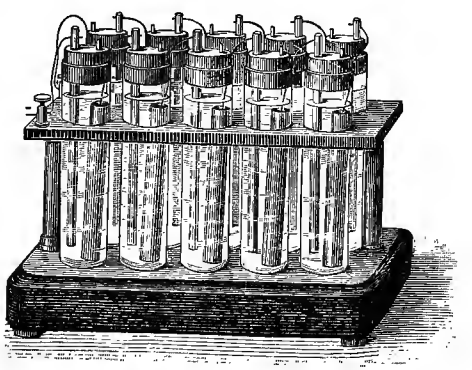


Fig. 25. — Silver Chloride Battery.

formed is capable of dissolving silver chloride, with the formation of ammonio-silver chloride. The hydrogen may reduce silver chloride with production of hydrochloric acid. This acid increases local action. Under such conditions gas may be liberated in the cell, and provision must be made for its escape; or the cell must be made very strong and must be securely sealed.

The initial E.M.F. of a silver chloride cell is about 1.1 volts. Its internal resistance falls very rapidly upon

first closing the circuit, on account of the reduced silver. It polarizes but slightly, and recovers promptly. It is employed chiefly for testing purposes; sometimes for physicians' use. But it should never be put into service requiring anything more than small currents. Upon standing, the zinc is liable to become coated with a thin, adherent film of the oxychloride of zinc, offering high electrical resistance.

44. Modifications of the Silver Chloride Cell. — The modifications thus far introduced consist in the substitution of some other exciting liquid for the ammonic chloride. Thus caustic potash or soda has been used by Scrivanoff. The chemical reaction is then the same as with the copper oxide cell, except that the hydrogen displaced by zinc unites with the chlorine of the depolarizer, forming hydrochloric acid. A secondary reaction is thus possible, due to the action of the acid on the zinc. There is then greater liability of local action than if the cell were set up with sal-ammoniac.

The excitant may also be zinc sulphate. The displacement process taking place is as follows: —

$$\overbrace{Zn_x \mid \underbrace{ZnSO_4}} \mid \overbrace{\underbrace{ZnSO_4} \mid \underbrace{2AgCl}} \mid \underbrace{Ag_y} =$$

$$Zn_{x-1} \mid ZnSO_4 \mid ZnSO_4 \mid ZnCl_2 \mid Ag_{y+2}.$$

In this case zinc chloride is formed at the expense of silver chloride, and the energy appearing in an electrical form may be represented as due to the difference between the heat of combination of zinc chloride and silver chloride.

The initial E.M.F. with caustic potash is 1.64 volts; with zinc sulphate, 1.16 volts; and with zinc chloride (Gaiffe), 1.01 volts.

It should be remarked that silver chloride is soluble to some extent in the chlorides of the heavy metallic elements. When the liquid contents of the cell contain as much as one part of concentrated zinc chloride in ten parts of water, the silver chloride is dissolved in quantities which are quite appreciable. Local action then ensues, due to the displacement of silver by zinc, and the zinc rod or plate quickly blackens.

The marked efficiency of silver chloride as a depolarizer is perhaps due to its slow or partial dissolving in the exciting liquid, since liquid depolarizers are, in general, more effective than solid ones. A weak solution of ammonic chloride may not attack the solid silver chloride. Hence local action does not take place so long as these cells have not been placed in use; but immediately upon closing the circuit through them zinc chloride is formed, and thereafter local action begins to exhaust the silver chloride with blackening of zinc. So that silver chloride cells that have been much used will not stand on open circuit without waste. Moreover, their internal resistance will increase if the zinc becomes encased in the film of oxychloride before mentioned.

CHAPTER V.

OPEN CIRCUIT BATTERIES.

45. The Leclanché Cell. — The present chapter will be devoted to open circuit batteries in which a solid depolarizer is used. At the head of this list stands the Leclanché cell, so called from the name of the inventor. Metallic oxides had been proposed as depolarizers previous to the invention of Leclanché, but without practical results. Thus, with zinc in dilute sulphuric acid and platinum surrounded with the peroxide of lead in a porous cup, Beetz found an E.M.F. of 2.4 volts. During 30 minutes short circuit this fell to 1.4, but recovered after five minutes rest to 2.16. It is evident that this high E.M.F. is due not only to the oxidation of the zinc, but to that of the hydrogen as well, both chemical processes contributing to the electromotive stress in the same direction.

The chief disadvantage in the employment of lead peroxide as a depolarizer lies in the fact that the reduced lead is converted into lead sulphate. This accumulates on the negative plate and has the effect of largely increasing the internal resistance of the cell.

It is worthy of note in this connection that one of the more recent forms of storage batteries is composed essentially of the elements used by Beetz; namely, zinc and lead in an acid solution of zinc sulphate.

The depolarizer of the Leclanché cell is manganese

dioxide (MnO_2). It is not used as a powder, but in granules mixed with broken gas carbon to increase the conductivity. The negative plate is baked carbon, and is surrounded with the mixed manganese dioxide and broken carbon, packed in a porous cup, which is finally sealed with pitch, with two small vent tubes inserted.

The typical Leclanché cell, with its porous cup (Fig. 26), has a glass jar moulded with a lip, in which is placed the zinc rod. The carbon plate is usually sur-

Fig. 26. — Leclanché Cell.

mounted with a lead cap, cast on the carbon, and holding the binding post of the positive terminal. The cut exhibits a new connection, designed to avoid corrosion of the lead cap.

The size of the zinc rod, which never exceeds half an inch (1.25 cm.) in diameter, indicates large internal resistance, and shows that this cell is designed to furnish only small currents through considerable external resistance. The amount of energy held potentially in the cell is represented approximately by the weight of the zinc.

The exciting liquid is ammonic chloride, the sal-ammoniac of commerce. To set up the cell, five or six ounces of best sal-ammoniac are dissolved in water. Water, or water containing sal-ammoniac, is also poured into the porous cup through one of the vent tubes. If water alone is added, the cell must stand for about 24 hours before use, to permit the diffusion of the ammonium salt through the porous cup, unless there are holes in it which allow the liquid to pass in rapidly.

An incidental advantage of this cell is that the diffusion of the liquid through the porous vessel, which serves only to hold the depolarizer and the broken carbon, is of positive utility; while in two fluid cells the diffusion of the two liquids through the pores is an undesirable feature.

The initial E.M.F. of the Leclanché cell varies from 1.4 to 1.7 volts, and the internal resistance from about 0.4 to 2 ohms.

46. Chemical Reactions in the Leclanché Cell. — Theoretically no chemical reactions take place so long as the circuit remains open, inasmuch as the cell contains neither acid nor an acid salt. But when the circuit is closed, zinc displaces ammonium from the ammonic chloride, and the ammonium breaks up into ammonia gas, which is set free and escapes after the liquid becomes saturated, and hydrogen which is oxidized by the manganese dioxide. These chemical changes may be represented by the following equation: —

$$\overbrace{Zn_x}\ |\ \overbrace{2NH_4Cl}\ |\ \overbrace{2NH_4Cl}\ \|\ 2MnO_2\ |\ C =$$

$$Zn_{x-1}\ |\ ZnCl_2\ |\ 2NH_4Cl\ \|\ 2NH_3\ |\ Mn_2O_3\ |\ H_2O\ |\ C.$$

If the liquid is allowed to become supersaturated by evaporation, a double salt of the chlorides of zinc and ammonium is liable to crystallize on the zinc. This reduces the E.M.F. and increases the internal resistance. A small quantity of hydrochloric acid will usually dissolve these crystals.

When a Leclanché cell is left undisturbed for some time, it will be found that the zinc rod is eaten away at the surface of the liquid, and that it is conical in shape, with the larger end of the cone at the bottom of the zinc. The excessive waste at the surface is doubtless due to oxidation, but the coning is the result of a peculiar local action sometimes seen in other forms of battery.

The double chloride of zinc and ammonium gradually settles to the bottom of the cell, becoming progressively denser and denser as the bottom is approached. Now zinc in a solution of ammonic chloride is positive to zinc in zinc chloride; if the latter liquid contains ammonic chloride also, the resulting E.M.F. is smaller, but still appreciable.[1] Hence local circuits are formed between the upper and lower portions of the zinc rod, the upper portions playing the part of the zinc in a simple voltaic combination.

The zinc plates of the copper oxide battery show a similar thickening from the liquid surface downward. The heavy zincate formed can be seen settling toward the bottom of the cell, and local action sets in, as already explained.

47. The Prism Leclanché Battery. — The prism form of the Leclanché cell was devised for the purpose of dispensing with the porous cup. The carbon plate is sus-

[1] See Experiments of Chapter IX.

pended from the cover (Figs. 27, 28), and attached to it by rubber bands are the two agglomerated prisms, containing the depolarizer. They consist of 40 parts granulated manganese dioxide, 52 parts granulated carbon, 5 parts gum shellac, and 3 parts acid potas-

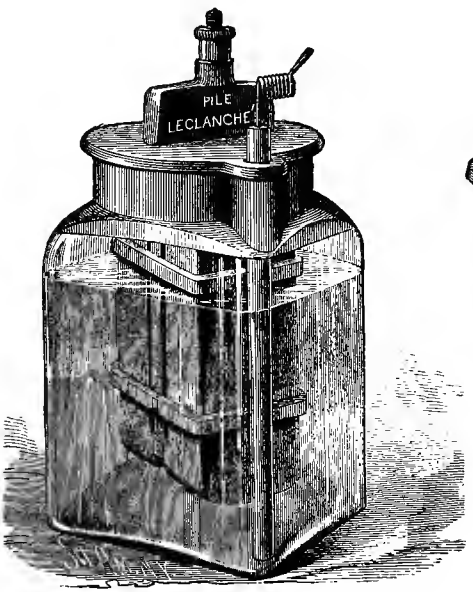


Fig. 27.

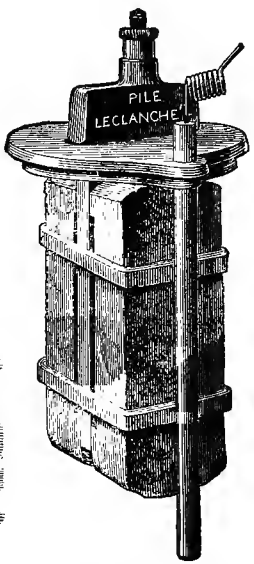


Fig. 28.

The Prism Leclanché Battery.

sium sulphate. The mixture is heated to 100° C., and then compressed in moulds under a heavy pressure.

This form of Leclanché cell has not met the expectations entertained at its first appearance. It appears not to be as efficient and durable as the original form, and has not come into general use in this country.

48. The Closed Leclanché Cell. — When an open Leclanché cell is kept in a dry place the liquid evaporates, and the solution becomes more concentrated, with greater liability of crystallization at the surface and consequent creeping of the salts upward toward the top. To avoid this difficulty, closed cells (of which Figs. 29 and 30 are examples) have been devised. In the former, the cover is wood sat-

Fig. 29.

Fig. 30.

Closed Leclanché Cell.

urated with paraffin and attached to the porous cup, but removable from the outer jar. So also the zinc is held loosely in the cover, and can be taken out. The cover fits down on a shoulder in the top of the jar, and a soft rubber ring makes it tight.

In the latter form the porous cup is made with a flange (Fig. 31), which rests upon the top of the jar.

Both the jar and the flange are paraffined, so that a close joint is made. The zinc passes through an opening in the cell specially provided for it. This is made tight by a piece of soft rubber tubing enclosing the rod at the point where it passes into the jar.

Two or three other modifications of details may be noted in these cells. In the one of Fig. 29, the porous cup, which is unusually large, has in the bottom three large holes covered with burlap. When the cell is set up, the sal-ammoniac solution enters at once, and the cell is ready for use.

Fig. 31.
Closed Leclanché Cell.

Fig. 32.—The Microphone Cell.

The porous cup (Fig. 31) has a small hole in the bottom to admit the liquid, and two holes, shown in the cut, on either side of the carbon at the top. The carbon has a special connection by means of a bolt and lock nuts, which serve their purpose satisfactorily.

A stop in the bottom of the glass jar prevents contact between the zinc and the porous cup. The two water marks on the jar serve as a convenient guide in filling. Each cell requires 4 oz., or 120 gms., of sal-ammoniac.

Both of these types of battery show an unusually

high E.M.F., and have done excellent service in the hands of the writer.

49. Leclanché Cells with Carbon Cup. — It is entirely practicable to dispense with the unglazed porous cup, and to make a carbon cylinder serve as a receptacle for the manganese dioxide. Two such cells are represented in Figs. 32 and 33. Both of these are loosely covered, to prevent evaporation, and have the depolarizer enclosed by carbon. The zinc of the latter is a cleft

Fig. 33. — Samson Battery.

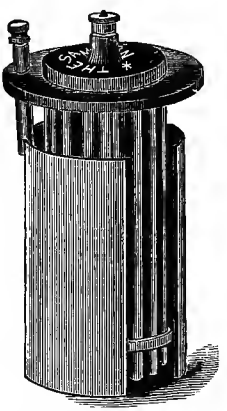


Fig. 34. — Zinc and Carbon.

cylinder (Fig. 34), and the carbon cup is corrugated to secure a larger surface. Both the polarization and recovery of these cells are not so rapid as in other forms of Leclanché cells, but they are more nearly continuous or uniform. A marked feature is the low internal resistance. It is only slightly over 0.3 ohm, and is no lower in the second than in the first, though the zinc cylinder has so much larger surface than the rod. The intervening distance is greater in No. 33, thus offsetting the larger surface.

With an external resistance of 5 ohms, the loss of potential in the interior of these cells is only 0.07 or 0.08 of a volt, or about 5 per cent of the total E.M.F. of the cell. They show, therefore, high commercial efficiency.

50. Leclanché Cell with Agglomerated Carbon. — In the cell shown in Fig. 35 the manganese dioxide appears to be incorporated with the carbon in the paste, and an agglomerate is thus produced by baking. This cell is effectively closed, and the zinc is insulated by a special glass sleeve passing through the carbon cover. A lug on the zinc rod fits into a corresponding socket in the glass, and serves the double purpose of holding the zinc up from the bottom of the cell and preventing its turning round when the connecting wire is screwed fast to the negative terminal.

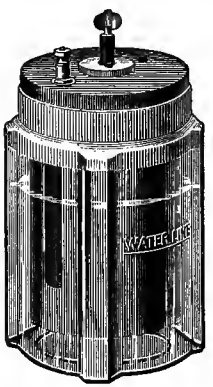


Fig. 35. — Cell with Agglomerated Carbon.

The agglomerated carbon cylinder has a long cleft on either side, and the zinc rod hangs in the centre. The glass insulator holds the zinc somewhat rigidly, and prevents any contact between it and the carbon.

This cell exhibits the same peculiarities of moderate but progressive polarization and good recovery as those of the last section. It has a somewhat higher internal resistance, which is, however, less than that of the ordinary Leclanché element.

51. Roberts' Peroxide Battery. — The elements are amalgamated zinc, carbon surrounded with an agglomerate of peroxide of lead, and a solution of chloride of

sodium, to which is added a small quantity of bichromate of sodium. The E.M.F. is 1.8 volts.

The agglomerate is made by adding minium (red lead) to powdered permanganate of potassium and hydrochloric acid, in quantity sufficient to form a semi-liquid paste. By the combined action of the acid and the permanganate, the Pb_2O_3 is converted into lead peroxide (PbO_2). The paste is then introduced into a mould containing a carbon electrode; and when after a few minutes it has set, it is withdrawn from the mould and dried at the temperature of the air. By this means a mass is obtained as dense as carbon.

The bichromate is added to the exciting liquid for the purpose of converting the chloride of lead in the agglomerate into an insoluble chromate. The partly soluble chloride would form a deposit of lead on the zinc.

In the action of the battery, zinc displaces sodium with the production of zinc chloride and sodium hydrate. Hydrogen is released in the formation of the hydrate, and this abstracts oxygen from the lead peroxide.

The internal resistance of such cells is large on account of the presence of insoluble lead salts.

52. The Sulphate of Mercury Battery. — Marié Davy first proposed the use of the sulphates of mercury as the depolarizing agent. For commercial purposes the acid sulphate is used, containing probably both the mercuric and the mercurous salts. These solids are only slightly soluble, and are therefore slow-acting depolarizers. The cell has various forms, but always contains zinc as the positive plate, and carbon, surrounded with the mercury salt, as the negative.

The form in which it is most used is for medical purposes. The carbon is at the bottom of a moulded rubber

case. On this is placed the mercurial salt with a little water. The amalgamated zinc plate is laid on top and is brought into contact with a platinum wire in the body of the rubber cell, and connection is thus made with the electrode. Usually two such cells are mounted together in series. The E.M.F. is about 1.45 volts.

53. The Fitch "Chlorine" Battery. — In Mr. Fitch's original battery the depolarizer was one of the chlorides of mercury; but in the process of improvement the chloride has been replaced by the chlorates of potassium and sodium. The excitant is composed of the chlorates of potassium and sodium and sal-ammoniac, "mixed in their proper combining proportions." Two forms, shown in Figs. 36 and 37, differ only in the extent of carbon surface exposed, and therefore in their internal resistance. The internal resistance of the form with carbon cylinder is about 0.35 ohm when the current flowing is 0.2 ampere, or with an external resistance of 5 ohms. Each package of the excitant weighs 145 gms., or 5 oz. About three-quarters of this is ammonic chloride, the remainder being the chlorates.

Fig. 36. — The Fitch Battery.

The larger cell requires four packages of excitant, each equal to the above. By accident, three of these cells were left on a closed circuit of 75 or 80 ohms for 2375 hours in long-distance telephone service. This is about 20 ohms per volt. During this three months service, their efficiency had not decreased sufficiently to be noticed in using the transmitter.

Fig. 37. — The Fitch Battery.

When this cell is exhausted by use, clean thoroughly the jar, the carbon, and the cover; and after drying, replace the zinc with a new one and supply a fresh solution of the excitant. The battery is then again ready for extended service.

In case of accidental short-circuiting, extreme cold, or very hard service, crystals of spent residue may form on the zinc and carbon. These may be removed by adding to each cell 1 oz., or 30 gms., of hydrochloric acid. More than this should never be added at one time, and then only when the accumulation on the plates demands it. Otherwise local action will take place on account of the presence of the acid.

CHAPTER VI.

BATTERIES WITHOUT A DEPOLARIZER.

54. The Smee Cell. — The oldest battery of any practical value without a depolarizer is the Smee (Fig. 38). The positive plates of this cell are zinc, enclosing between them, with proper insulation, a negative of thin silver, corrugated and covered with platinum in a very finely divided state. The excitant or electrolyte is dilute sulphuric acid; and the purpose of the roughened surface of the silver is the mechanical dislodgement of the hydrogen as fast as it is released at the negative plate, since hydrogen is found to be much more easily detached from a rough surface than from a smooth one.

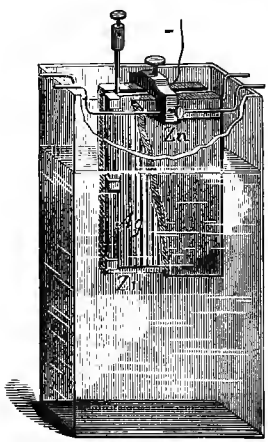


Fig. 38. — The Smee Cell.

The silver plate may be prepared as follows: Obtain thick silver foil and roughen the surface lightly with fine glass-paper, or by brushing over with strong nitric acid. Unless the surface is roughened the platinum black will not adhere. Connect the silver plate, by means of a copper wire, with a small slip of zinc, and insert the silver in a vessel of dilute

acid, to which has been added a few drops of platinic chloride. The zinc slip should then be merely touched to the dilute acid at a point remote from the silver. The slight current thus produced will be sufficient to decompose the platinic chloride, and the platinum will gradually deposit on the silver and color it. Then add more of the platinum salt, and insert the zinc deeper into the liquid. Gradually increase the current till the surface of the silver plate is covered with a black coating of finely divided platinum.

The platinic chloride may be prepared by dissolving scrap platinum in a mixture of two parts hydrochloric acid to one of nitric acid, and gently warming for some time. For the above use it is not necessary to drive off the acid or to crystallize the salt.[1]

A negative plate for the Smee cell has been formed of copper, with the surface roughened by electro-deposition, then plated with silver, and finally platinized. It is said, however, that the silver plating is liable to be porous, and that the acid in time works through to the copper. Also, that the copper dissolves at the edges and is deposited again on the silver.[2]

55. The Sea Salt Battery. — A battery which is said to have done good service has been made with sea salt and powdered alum, in the ratio of five parts to two, dissolved in water, as the excitant. The elements were zinc and carbon, the latter having a very large surface. Zinc chloride and zinc sulphate are formed, and hydrogen is set free, with formation of sodium and potassium hydrates.

Exactly what part the alum takes in the reactions is uncertain and obscure. But such cells are capable of

[1] Sprague's Electricity, p. 92. [2] Phil. Mag., May, 1840.

intermittent service for certain classes of work requiring only small currents.

56. The Law Battery. — In this battery, and in others of similar design, reliance is placed upon a large carbon surface to effect depolarization mechanically. The negative consists of a double cleft cylinder of carbon, with the zinc rod hanging well within the cleft (Fig. 39). The carbon has a surface of about 145 square inches, and the internal resistance is 0.4 ohm when the current flowing is 0.2 ampere. The cell is effectively closed by an insulating cover, so made that by a partial turn it locks down tightly against a soft rubber ring. The jar is of flint glass, annealed, and its capacity is one and one-third quarts, or one and a half litres. Sal-ammoniac is the excitant, and each cell takes one litre of the solution containing 150 gms., or 5 oz., of the salt.

Fig. 39. — The Law Battery.

A renewal of an exhausted cell requires only a new zinc rod and a fresh solution of sal-ammoniac. The spent solution should always be thrown out, and the double carbon cylinder should be thoroughly soaked in water and then exposed to the sun and air, to remove the absorbed salts.

This cell is neat, clean, durable, and efficient. For hard work it polarizes more continuously than a Leclanché cell, but for light currents the polarization is not sufficient to be noticeable. The initial E.M.F. is 1.37.

57. The Diamond Carbon Battery. — The negative of this cell is composed of seven rods of soft carbon, 5.5

inches long and five-eighths of an inch in diameter, set into a soft metal top and secured by a set screw, in the manner shown in Fig. 40. The metal top is cast round a porcelain insulator through which passes the zinc rod. The zinc is kept from falling too low by an iron cross-pin, and a rubber ring closes the annular opening in the

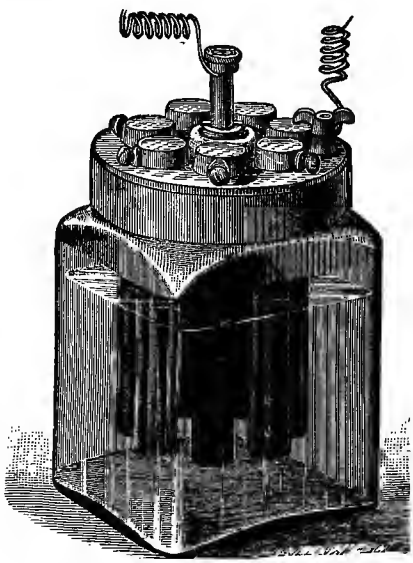


Fig. 40. — "Diamond" Carbon Battery.

porcelain round the zinc. Another rubber ring at the bottom of the zinc prevents contact with the carbons. The tops of the cells are covered with paraffin or bees-wax; the inside of the cover and the upper ends of the carbons are also paraffined. Care should be taken not to allow any of the solution of the sal-ammoniac to get on the cover, otherwise the crystallization and creeping

of the salts produce a short circuit, and the cell exhausts itself on apparently open circuit.

The internal resistance is only about 0.25 ohm, with 5 ohms external resistance; the polarization is continuous and progressive, as in all cells of this class, but the recovery is very good. The initial E.M.F. is 1.36 to 1.39 volts.

58. Cylinder Carbon Batteries. — In addition to the cylinder carbon battery already described, attention may be drawn to two others (Figs. 41 and 42). In the former, the carbon cylinder and cover of the jar are made in one piece, and the cylinder in both is cleft for free diffusion of the sal-ammoniac solution. The oval form of the Laclede (Fig. 42) has no advantage, except increased carbon surface. The connection with the binding post is made in both cases in such a way as to render corrosion by capillary ascent of the liquid quite remote. A greater danger in all these cells arises from careless handling after they are set up, during which the liquid splashes up against the top and over the porcelain insulating the zinc. The initial E.M.F. of all carbon cells without depolarizer appears to be about the same, — between 1.3 and 1.4 volts. They quickly drop below this value with a current of two-tenths of an ampere, and subsequently rise but little above a single volt. The ease and cheap-

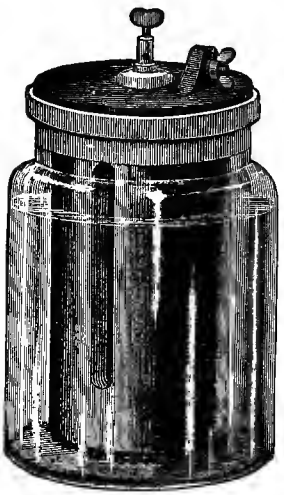


Fig. 41. — The Cylinder Cell.

ness with which they may be restored to nearly their initial efficiency after exhaustion constitute a strong commendation in their favor.

Fig. 42. — The Laclede Battery.

59. The Gassner Dry Battery. — A large part of the most recent batteries appearing as candidates for public favor are of the so-called dry type. They contain the excitant in the form of a paste, the composition of which is in most cases a secret. Their convenience commends them to those having no technical knowledge relating to batteries, and they are very useful in situa-

tions precluding the use of unsealed cells with liquid electrolytes. But their store of available potential energy is, in general, smaller than that of batteries containing a larger quantity of fluid.

One of the oldest cells of the dry type is that of Dr. Gassner (Fig. 43). The zinc, composing the positive element, is the containing vessel. It is usually covered with paper, or is enclosed in a paper box. The negative element is carbon, and it occupies about one-half the space in the cell.

Fig. 43. — Gassner Dry Cell.

The paste, which is filled in between the zinc and the carbon in the Gassner cell, has the following composition: "Oxide of zinc, 1 part, by weight; sal-ammoniac, 1 part, by weight; plaster, 3 parts, by weight; chloride of zinc, 1 part, by weight; water, 2 parts, by weight. The oxide of zinc in this composition loosens and makes it porous, and the greater porosity thus obtained facilitates the interchange of the gases and diminishes the tendency to the polarization of the electrodes."

The initial E.M.F. of this cell varies but little from 1.3 volts. It polarizes very rapidly on so low an external resistance as 5 ohms; while the internal resistance, which is different for cells of different size, is very irregular during the working of the cell, probably on account of the slow and irregular diffusion of the products of the chemical action.

Such cells should be employed for intermittent service, where the circuit is kept closed for short periods only. In such situations they will doubtless prove efficient and durable. Their convenience, particularly in the hands of unskilled persons, is much in their favor.

Meserole's composition for a dry battery is the following: —

Charcoal, 3 parts; mineral carbon or graphite, 1 part; peroxide of manganese, 3 parts; white arsenic oxide, 1 part; a mixtnre of glucose and dextrine or starch, 1 part; hydrate of lime, dry, 1 part — all by weight.

These are intimately mixed and worked into a paste of proper consistency with a solution composed of equal parts of a saturated solution of chloride of ammonium and common salt, to which are added one-tenth of the volume of a solution of bichloride of mercury and an equal volume of hydrochloric acid. The fluid is added to the dry mixture gradually, and the mass is well worked to insure uniformity.

CHAPTER VII.

STANDARDS OF ELECTROMOTIVE FORCE.

60. Latimer Clark's Standard Cell. — The original Latimer Clark normal element was described for the first time in a paper read before the Royal Society, June 19, 1873.[1] The metallic elements are pure zinc in zinc sulphate, and pure mercury in contact with mercurous sulphate (Hg_2SO_4). The mercury was placed in the bottom of the cell, and contact was made with it, either by passing a platinum wire down through a small glass tube in the cell itself, or else through one blown on the cell near the bottom.

The zinc sulphate solution was made by boiling an excess of pure zinc sulphate crystals in distilled water, and decanting the clear solution off from the crystals after cooling.

On the mercury was poured a thick paste, made by boiling mercurous sulphate with the solution of zinc sulphate, saturated in the manner just described. Into this paste dipped a zinc rod, or else a plate of pure zinc rested on its surface. Special stress was placed on the boiling of the paste with zinc sulphate solution for the purpose of expelling the air.

The cell was imperfectly sealed with a paraffin stopper.

[1] Philosophical Transactions, 1874.

The normal E.M.F. of this cell, according to Clark, was 1.457 volts. But this was on the basis of the British Association (B.A.) unit of resistance. Now the unit of E.M.F. varies directly as the unit of resistance. If, therefore, the true ohm, which is represented, according to our latest knowledge, by the resistance of a column of pure mercury of one square millimetre cross-section, and 106.3 cm. long at 0° C., is 1.014 times the B.A. unit, then the true volt is also 1.014 times the B.A. volt. Hence, to reduce 1.457 B.A. volts to true volts, divide by the above ratio. The result is 1.437 true volts. This is only 0.002 volt higher than the later value assigned by Lord Rayleigh, as the result of his extended observations.

61. Lord Rayleigh's Form of the Clark Element. — The original Clark cells exhibited certain abnormal and irregular values both of E.M.F. and temperature coefficient. A thorough investigation of the Clark cell was therefore undertaken by Lord Rayleigh, and the results were published in the "Philosophical Transactions of the Royal Society," Part II., 1885, under the title of "The Clark Cell as a Standard of Electromotive Force." This paper was supplementary to one published in the same place in 1884 on "The Electro-Chemical Equivalent of Silver, and the Absolute Electromotive Force of Clark Cells." Only a brief summary of results of this very important investigation can be given here.

The E.M.F. of a Clark cell may be too high (1) because the paste is acid; (2) because the zinc sulphate solution is not saturated. The first fault will cure itself in the course of a month or so.

The E.M.F. may be too low (1) because the cell has become dry; (2) because the solution is supersaturated;

(3) because the mercury is not pure. The cell loses liquid because of imperfect sealing. Paraffin cracks away from the glass. Lord Rayleigh recommends marine glue. Supersaturation results from heating the solution or the paste. The strong solution will then cool without any deposit, or will throw down an abnormal hydrate. The presence of crystals does not prove that the solution is not in the state of supersaturation, unless it can also be proved that these crystals are those of the normal hepta-hydrated salt. The addition of a few crystals of the normal zinc sulphate will always cause the excess of salt held in solution at a given temperature to crystallize out.

Respecting the presence of other metals in the mercury, it is sufficient to notice only that of zinc. Zinc opposed to pure mercury, without the presence of Hg_2SO_4, gives an uncertain E.M.F. of about 1.186 volts. But when the mercury contains one part of zinc in 5,900,000, the E.M.F. falls to 0.513 volt; and with one part zinc in 200,000 it becomes only 0.124 volt.[1]

With zinc opposed to pure mercury in a zinc sulphate solution, the E.M.F. is not constant from hour to hour, and is altered by the passage of a minute quantity of electricity which would be insufficient to produce the least effect upon a cell provided with mercurous sulphate. So marked is the action of the mercurous sulphate in repurifying the mercury, that Lord Rayleigh suggests that this may be its principal office in the Clark cell; and he attaches the greatest importance to purity of mercury. "It is clear," he says,

[1] "On the Electromotive Force of Mercury Alloys," Journal Society Telegraphic Engineers, Vol. VIII, 1879.

"that the mercurous sulphate has the property of freeing the mercury from the smallest contamination with zinc."

Lord Rayleigh's cell (Fig. 44) is made as follows: A small tube has a platinum wire sealed through the closed end. On this is poured enough pure mercury, distilled **in vacuo**, to cover the platinum effectively. The paste which covers the mercury is prepared by rubbing together in a mortar 150 gms. mercurous sulphate, 5 gms. zinc carbonate to neutralize acid, and as much zinc sulphate solution, saturated by standing in a warm place, as will make a thick paste. After the carbonic acid gas has escaped, this paste is poured into the tube through a small funnel, care being taken not to soil the sides of the tube. After adding a few crystals of zinc sulphate to insure saturation, the cleaned zinc rod, with a copper wire soldered to its upper end, is passed down into the paste, and is held in position by a piece of cork which nearly touches the paste. Finally, enough hot marine glue is poured in to cover the zinc and cork, and to leave only the wire projecting. The figure shows the cross-section of such a cell. In no stage of the process is heat applied to the paste. In this particular, Lord Rayleigh's procedure is in marked contrast to that of Latimer Clark.

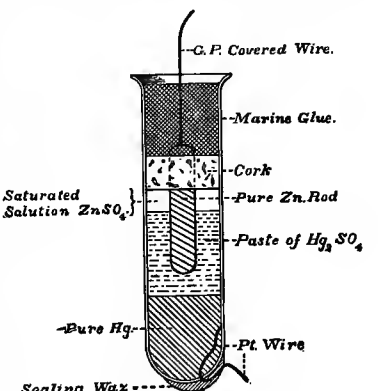


Fig. 44. — Rayleigh Standard Cell.

The E.M.F. of a Clark cell, constructed as above, Lord Rayleigh found to be 1.435 true volts. This is equal to 1.438 legal volts, corresponding with the legal ohm, or to 1.455 B.A. volts at 15° C.

Using a silver voltameter as a secondary standard, the writer found a Clark cell, made in Berlin after Latimer Clark's directions, to have an E.M.F. of 1.437 legal volts at 15° (strictly 1.434 at 18° C.).

The value of the temperature coefficient was also investigated by Lord Rayleigh. It was found to vary considerably for different individual cells; but for cells with **saturated solutions** the following equation can lead to no appreciable error: —

$$E = 1.435\,\{1 - 0.00077\ (t - 15)\}:$$

t is the temperature of the cell.

Latimer Clark found a temperature coefficient of 0.06 per cent per degree C. for temperatures within 10° on either side of 15. For higher temperatures he observed a diminution of the coefficient; so that for the whole range of observations, extending up to 100° C., the coefficient was 0.055 per cent per degree C.

62. A Standard Clark Cell with Low Temperature Coefficient. — The objections to Lord Rayleigh's form of the Clark normal element are: (1) the temperature coefficient is high and apparently variable; (2) it is not constructed in such manner as to keep the zinc and metallic mercury out of contact; (3) the contact of the zinc and the mercurial salt permits of local action whereby zinc replaces mercury.

Respecting the first objection, the method to be pursued in reducing the temperature coefficient is suggested by the fact, now well known, that the E.M.F. decreases

with an increase in the density of the zinc sulphate solution. Hence, if the solution is saturated at 30° or 40°, upon a lowering of temperature the excess crystallizes out with a decrease of density. The reverse process takes place with rise of temperature, with the additional disadvantage that time is required for the diffusion of the redissolved salt. The temperature coefficient in such a cell is therefore made up of two parts: one a real temperature effect, the other a secondary change resulting from a variability in the density of the zinc sulphate solution. A rise of temperature lowers the E.M.F. by increasing the density of the solution in addition to the direct primary effect of the temperature change.

The slowness of diffusion when the temperature rises makes the coefficient for a rapid rise of temperature smaller than for a slow one. Thus Professor Threlfall,[1] investigating Clark cells made in accordance with Lord Rayleigh's directions, found the coefficient to be 0.000402 for a rapid rise of temperature from 21° to 34° C. This is less than half the value found by Lord Rayleigh between the same temperatures.

The magnitude of the temperature coefficient depends, then, upon the temperature at which the zinc salt is saturated; and, because of diffusion, upon the rapidity of the temperature change. To obviate these difficulties the zinc sulphate should be saturated at some definite temperature lower than any at which the cell is to be used. The temperature selected by the writer is that of melting ice.

The following table exhibits the observed and calcu-

[1] Philosophical Magazine, November, 1889.

lated values of the E.M.F. of a cell, set up with such a solution, in terms of a Rayleigh cell at 20° C.: —

Temperature C.	Observed.	Calculated.
°		
8.3	1.0108	1.0106
8.5	1.0103	1.0105
9.3	1.0104	1.0102
11.8	1.0093	1.0092
13.8	1.0084	1.0085
15.0	1.0080	1.0080
18.1	1.0069	1.0068
19.4	1.0064	1.0063
19.9	1.0062	1.0061
20.3	1.0060	1.0059
20.8	1.0054	1.0057
21.1	1.0057	1.0056
21.6	1.0054	1.0055
22.4	1.0050	1.0052
23.3	1.0048	1.0048
25.1	1.0044	1.0041
26.4	1.0035	1.0036
30.2	1.0019	1.0022
33.1	1.0014	1.0013
39.1	0.9991	0.9989
41.7	0.9980	0.9979
50.4	0.9949	0.9947
52.7	0.9939	0.9940

The Rayleigh cell was always very near 20° C., and the reduction to that temperature was made by means of the coefficient 0.00077.

The equation for the E.M.F., derived from the above observations, is —

$$E_t = E_{15} \{1 - 0.000387\ (t - 15) + 0.0000005\ (t - 15)^2\}.$$

The calculated values of the second column were all obtained by this formula. The change for one degree C. is the following linear function of the temperature: —

$$-0.000386 + 0.000001\,(t - 15).$$

The coefficient ranges from 0.00040 at 0° to 0.000376 at 25°, and 0.000361 at 40° C. At the highest observed temperature of the table it was only 0.000348. The

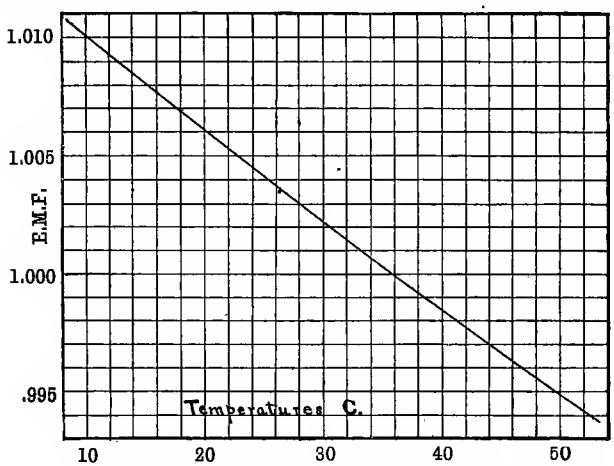


Fig. 45. — Relation between E.M.F. and Temperature.

curve of E.M.F. with temperatures as abscissas is clearly concave upward (Fig. 45), indicating a fall in the temperature coefficient with rise of temperature. Lord Rayleigh's cell showed a considerable increase in the coefficient with rise of temperature, the sign of the second term in his equation expressing the relation between E.M.F. and temperature being negative.

The other two objections urged against the usual form of Clark cell are founded chiefly on the local

action taking place when the zinc and mercurial salt are in contact. Zinc replaces mercury to some extent when in contact with a salt of mercury. With the oxide of mercury this action is very marked, resulting in reduction of the mercury and oxidation of zinc. The same replacement process goes on with mercurous sulphate, zinc sulphate being formed at the expense of zinc and mercury sulphate, while the zinc is amalgamated with the reduced mercury. A progressive change in the density of the solution ensues, entailing perhaps a rise in the value of the temperature coefficient.

It may be noted, further, that if the cell contains crystals of zinc sulphate, the liquid at the surface of the mercury salt in an undisturbed cell is likely to be denser than it is even a few millimetres higher up, because the zinc sulphate crystals form at the bottom of the liquid. Bearing in mind that zinc in dilute zinc sulphate is positive to zinc in a relatively denser solution, it is easy to see that a voltaic couple is thus formed of one metal and two solutions of different densities. That this is actually the case is proved both by experiment[1] and by the deposit of zinc on the zinc rod just at the surface of the mercurous sulphate. Upon dismounting and opening one cell, which was perhaps a year old, it was found that zinc had been removed from the rod at the surface of the liquid, and some of it had been deposited again upon the rod at the surface of the mercury salt in a solid frill, which was not easily detached. This action is analogous to the transfer of copper from one plate to another in electrical connection with it, when the two are immersed in a solution of copper sulphate, and the temperature at one plate is kept higher than at the other.

[1] See Chapter IX.

The obvious remedy is to insert a porous partition between the mercurous sulphate paste and the zinc in zinc sulphate solution.

For cells not intended for transportation, plaster of paris, mixed up with a somewhat dilute solution of zinc sulphate, answers perfectly. Its effect on the E.M.F. appears to be nil. But if much disturbed it is liable to break up after a few months. A slip of cork is better if the cell is to be roughly shaken, as in transportation. The separation of the zinc from the mercury salt increases the E.M.F. about 0.4 per cent, or from 1.435 to 1.440 true volts at 15° C. Since mercurous sulphate is almost insoluble in concentrated zinc sulphate, the separation of the zinc from the mercury salt appears to present a complete mechanical obstacle to local action. This view is confirmed by observations on cells two years old.

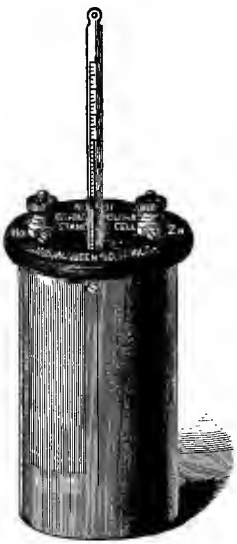


Fig. 46.
Carhart-Clark Standard Cell.

To prevent accidental short circuits, it is desirable to mount a standard cell with a high resistance in series with it. This resistance of about 10,000 ohms, consisting of plumbago on glass, is mounted in the case (Fig. 46), and is, therefore, always in circuit with the cell. It can give rise to no error so long as zero or condenser methods are employed.

63. The Oxide of Mercury Standard Cell. — This normal element was described by M. Gouy in the "Journal de Physique," Tom. VII., 1888, p. 532. M. Gouy employs

the oxide of mercury instead of the sulphate as a depolarizer. He further makes use of a 10 per cent solution of crystallized zinc sulphate, of density 1.06, in place of a saturated one.

M. Gouy finds that the negative polarization of his cells, due to closing the circuit, does not amount to one one-thousandth of the E.M.F. after the cell has been agitated and left standing for a short time.

On the other hand, the positive polarization, arising from a reverse or charging current, persists longer than the negative. It can be gotten rid of by closing the circuit for a short time to produce negative polarization, from which the cell rapidly recovers. The reverse current undoubtedly forms some mercurous sulphate, which gives a higher E.M.F. as a depolarizer than the oxide; and, while it lasts, produces an apparent polarization in the positive sense.

The E.M.F. of this cell is 1.390 legal volts at 12° C., and the change due to temperature is 0.0002 volt per degree. The formula for the E.M.F. is then

$$E_t = 1.390 - 0.0002\ (t - 12).$$

This is equivalent to a temperature coefficient of 0.000104, or only about 0.01 per cent per degree C.

The E.M.F. of this cell is said to increase with increase of density of the zinc sulphate solution.

To prevent local action, the zinc is not allowed to come in contact with the mercuric oxide. For use in which high internal resistance is of no consequence, the zinc rod is placed in a glass tube having in it a small hole near the lower end. If it is necessary to decrease the internal resistance, the zinc is enclosed in a linen bag.

Detailed directions are given for the preparation of

zinc sulphate and mercuric oxide; also for the purification of zinc and mercury.

64. Sir William Thomson's Standard Daniell Cell.— Some form of Daniell cell has long been used as a standard of E.M.F., partly because its polarization is small, and partly because its E.M.F. is near unity. To insure constancy, some provision must be made to prevent, or at least to greatly retard, the mingling of the two sulphates. Thus Raoult's cell consists of two glass vessels, one containing zinc in zinc sulphate, and the

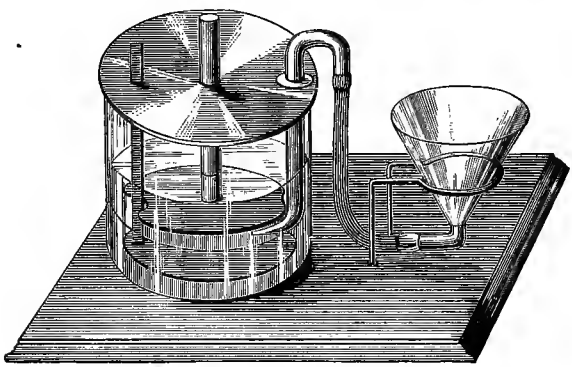


Fig. 47. — Thomson Standard Daniell Cell.

other copper in copper sulphate. When in use the two vessels are connected by an inverted U-tube, filled with zinc sulphate solution, and closed at both ends with a piece of thin bladder.

The normal Daniell element of Sir William Thomson (Fig. 47) consists of a rather low glass jar, with a plate of zinc in saturated zinc sulphate solution at the bottom. Above is suspended the copper plate; and the copper sulphate, which is a half-saturated solution, is introduced through the funnel, connecting by a rubber tube to a

siphon which terminates in a pointed horizontal tube at the surface of the zinc sulphate. By filling the funnel and gently raising it, the copper sulphate will flow over the surface of the saturated zinc sulphate, so that the surface of separation between the two liquids will be clearly defined. Upon the termination of the experiment the funnel is lowered and the solution is run out. It should be used but once. Just before making quantitative use of the cell a feeble current should be sent through for a short time to freshly coat the copper plate.

The E.M.F. of a cell thus set up has been found to be 1.072 true volts at about 15° C. The temperature coefficient is small, but appears not to have been carefully determined. Dr. Fleming found it to be about one-fifth of the variation of the Rayleigh-Clark cell between 0° C. and 20° C.;[1] but Mr. Preece found a greater variation, amounting to 9 parts in 1000, for one-half the range of temperature, or between 17° and 28°.[2] If Mr. Preece is correct, the temperature coefficient of the normal Daniell cell within the above range is quite as high as that of the Rayleigh form of Clark element. Mr. Preece's method was scarcely sensitive enough to admit of a good determination of the variation of E.M.F. with temperature.

65. Lodge's Standard Daniell Cell. — A wide-mouthed bottle (Fig. 48) is provided with a cork, through which passes a large test-tube R with a small opening at the bottom. The zinc rod Z is held in this tube by a cork. A small test-tube c is fastened to R by an elastic band. This tube contains the solution of copper sulphate, and into it dips a gutta-percha covered copper wire, bared at

[1] Philosophical Magazine, August, 1885, p. 136.

[2] Proceedings Royal Society, Vol. XXXV. 1883, p. 48.

the lower end and furnished with a fresh deposit of electrolytic copper. The insulated wire passes through a cork in the small tube. This tube is immersed in the zinc sulphate solution contained in the bottle G up to a point near its top.

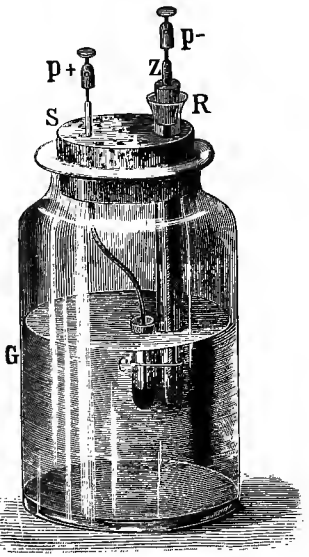


Fig. 48.
Lodge's Standard Daniell Cell.

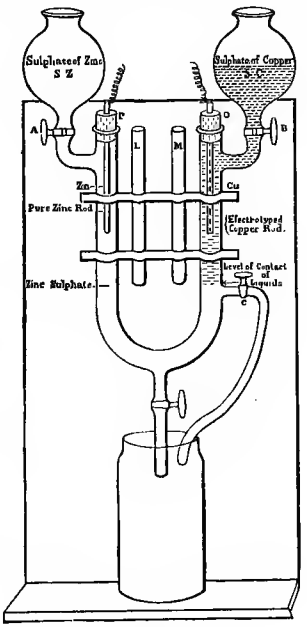


Fig. 49.
Fleming's Standard Daniell Cell.

The two sulphates are by this device kept entirely separate, and the electric connection between them is established by means of the moisture covering the glass.

The internal resistance of the element is enormously high, and the cell is applicable only to zero methods or comparisons by means of a condenser.

66. Fleming's Standard Daniell Cell. — The form of Daniell cell shown in Fig. 49 was specially designed

by Dr. Fleming as a standard of E.M.F.[1] It consists of a U-tube 8 inches long and $\frac{3}{4}$ inch in diameter, provided with side tubes, glass taps, and reservoirs as shown.

To fill the cell, the tap *A* is opened, and the tube is filled with the denser zinc sulphate solution. *A* is then closed, and the zinc rod is secured in the left-hand branch by means of an air-tight rubber stopper *P*. The tap *C* is now opened, and the liquid falls in the right-hand branch only; and if the tap *B* is opened at the same time, the copper sulphate solution will flow in gently as the level of the zinc solution sinks in this branch. The operation may be so conducted that the surface of separation between the two solutions will remain quite sharp, and will gradually sink to the level of the tap *C*. All the taps are then closed, and the copper rod is inserted in the right-hand limb.

When the surface of contact ceases to be sharply defined by reason of diffusion, it is only necessary to draw off the mixed liquid at the level of the tap *C*, and to supply fresh solutions from the reservoirs above. The extra tubes, *L* and *M*, are for the purpose of holding the electrodes when not in use, each in its own solution.

The exact value of the E.M.F. of a Daniell cell is dependent upon the density of the solutions and the condition of the zinc and copper surfaces. Thus

Increase in density of the $CuSO_4$ solution increases E.M.F.
Increase in density of $ZnSO_4$ solution decreases E.M.F.
Oxidation of the copper surface increases E.M.F.
Oxidation of the zinc surface decreases E.M.F.

Moreover, for an equal increment or decrement of density of both solutions the increment and decrement

[1] Philosophical Magazine, 5 S., Vol. XX. p. 126.

of the E.M.F. are so nearly equal, that for equi-dense solutions, within limits, the E.M.F. is independent of the absolute density of either.

It is of the utmost importance that oxidation of the copper surface should be carefully guarded against. Even slight oxidation, indicated by brown spots, raises the E.M.F. by as much as 4 parts in 1000, while a film of dark brown oxide may affect the E.M.F. as much as 2 per cent. Since rolled copper sheets or drawn wire probably enclose more or less oxide mechanically, it has been found necessary to freshly electroplate the copper surface immediately before use. Raoult found that copper foil gave a higher E.M.F. than electro-deposited copper by about one two-hundredth; and he attributed it to the oxides of copper enclosed in it. If a newly electroplated copper rod is left in the copper sulphate solution, it is gradually oxidized; and the oxidation is more rapid if the rod is exposed to the air and contains even a trace of the copper sulphate. The rod should be electroplated with a thin film of copper immediately before it is transferred to the standard cell for use.

If a chemically pure zinc rod is used, it is immaterial whether it is amalgamated with pure mercury, or is freed from oxide on the surface by slight rinsing in dilute sulphuric acid before placing it in the sulphate of zinc.

For general use Fleming recommends two standard solutions of each salt. First, a solution of copper sulphate, saturated at 15° C., and of density 1.2, and a solution of zinc sulphate of the same density. Second, a solution of the copper salt, of density 1.1 at 15°, and one of the zinc salt, of density 1.4 at the same temperature.

If equi-dense solutions are used, with the precautions already described respecting the surfaces of the zinc and copper rods, the E.M.F. is very close to 1.102 true volts.

If, however, copper sulphate of density 1.1 and zinc sulphate of density 1.4 are used, then the E.M.F. of the cell is 1.072 volts. These last solutions correspond with those employed by Sir William Thomson in his standard form of gravity cell.

If the cell is allowed to stand an hour or so after the freshly electroplated copper pole is introduced into it before measuring the E.M.F., then its value will be about 0.003 volt higher than the above, provided the zinc retains a bright untarnished appearance. But the smallest deposit of copper on the zinc, due to the diffusion of the copper salt into the zinc sulphate, lowers the E.M.F. 2 or 3 per cent.

The many precautions required to insure a normal E.M.F. in a standard Daniell cell, on every occasion of its use, are more than an offset to a negligible temperature coefficient in comparison with that of a Clark cell, particularly if the latter is reduced to 0.038 or 0.039 per cent.

67. The Chloride of Lead Standard Cell. — MM. Baille and Féry have proposed[1] the use of a salt of lead as a depolarizer. The best results were obtained with the chloride. It has one of the disadvantages of the Daniell, but in an inferior degree; that is, the deposition on the zinc of the metal contained in the depolarizer. But with proper precautions, the formation of this metallic deposit may be greatly retarded.

The cell is mounted as follows: Powdered lead

[1] Journal de Physique, Tome IX. p. 234.

chloride, precipitated from a warm solution and of crystalline texture, is introduced into the tube *A* (Fig. 50) which encloses a lead wire, forming the negative of the element. The positive is a plate of zinc, amalgamated and immersed in a solution of chloride of zinc, of density 1.157.

When the circuit is closed zinc is dissolved, and chloride of lead is reduced.

The E.M.F. decreases with the concentration of the zinc chloride solution. With the above density, made by dissolving 17.2 gms. pure zinc chloride in 100 c.c. distilled water, the E.M.F. is exactly one-half a volt. Dr. Fleming's standard Daniell cell was taken for comparison.

The variation of E.M.F. with temperature was found to be almost negligible, amounting to only 0.005 volt in 46° C.

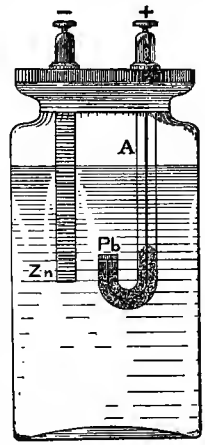


Fig. 50. — Chloride of Lead Standard Cell.

The solution of zinc chloride should be made neutral by agitation with zinc oxide, since the presence of free acid augments the electromotive force.

The polarization, though greater than in the Daniell cell, is still very small, and the cell recovers promptly and exactly its normal value.

68. To Measure the E.M.F. of a Standard Cell. — In the absence of means of making an absolute determination of the E.M.F. of a standard cell, the silver voltameter may be resorted to as a secondary standard. Of this method, Lord Rayleigh remarks: "It will be seen

that in this way any one may determine the E.M.F. of his standard battery with a very moderate expenditure of trouble, and without the need of any special apparatus."[1]

The method of making the determination is shown in Fig. 51. The main battery B is a storage cell, and in series with it is a carefully adjusted resistance SR of 10 legal ohms at 14° C., made of platinoid wire immersed in kerosene; also a silver voltameter V, and a second resistance R of heavy iron wire for the purpose of adjusting the current to the proper value. The standard cell B' is placed in a derived circuit at the terminals AC of the 10-ohm coil. In circuit with it is a sensitive "long coil" galvanometer G, and a carbon resistance, HR, of 100,000 ohms. A balance is effected between the E.M.F. of the standard and the fall of potential over the 10-ohm coil by varying the auxiliary iron resistance, and by greater or less immersion of the vertical silver plates of the voltameter in the silver nitrate solution. If any small change occurs in the current during the deposition of the silver, the balance may be maintained perfectly by changing slightly the depth of immersion of the silver

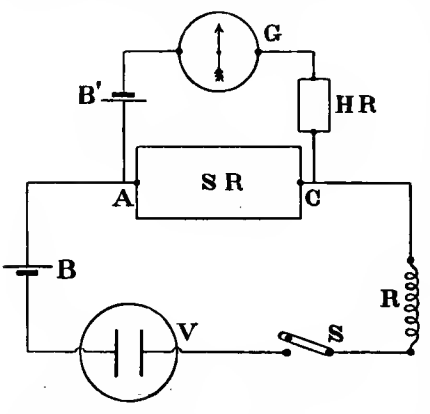


Fig. 51.—E.M.F. Measured by Silver Voltameter.

[1] Philosophical Transactions, Part II. 1884, p. 453.

plates. For this purpose the voltameter is provided with a rack-and-pinion movement for the plates.

All the conditions for a balance being ascertained, the gain plate is carefully washed, dried, and weighed. It is then replaced, and the circuit is kept closed for a sufficient time to secure enough gain in the kathode plate to weigh accurately, the balance being carefully maintained as described during the entire time. The gain plate is again removed, and the amount of silver deposited is determined. This gives the value of the mean current through the 10-ohm coil. Then by Ohm's law, $E = CR$; and since both current C and resistance R are known, E is in this manner determined.

Example.

Temperature of standard cell, $\frac{1}{2}(15°.5 + 15°.7) = 15°.6$ C.
Temperature of 10-ohm coil, $\frac{1}{2}(16°.6 + 16°.7) = 16°.65$ C.
Resistance of 10-ohm coil at $16°.65 = 10.00583$ legal ohms.

Weight of silver plate after deposit, . . .	29.99292 gms.
Weight of silver plate before deposit, . .	29.79942 "
Weight of silver deposited, ...	0.1935 "

Time of deposition, 20 minutes.
1 ampere deposits 4.0246 gms. per hour.

Hence the current equals

$$0.1935 \div \tfrac{1}{3}(4.0246) = 0.14424 \text{ amperes,}$$

and

$$E = 0.14424 \times 10.00583 = 1.44324 \text{ legal volts at } 15°.6 \text{ C.}$$

Reducing to 15° by the formula

$$1.4432 = E\,[1 - 0.000386\,(t - 15)],$$

the E.M.F. of the standard equals 1.4435 legal volts.

CHAPTER VIII.

MISCELLANEOUS BATTERIES.

69. Grove's Gas Battery. — The polarization current obtained from a water voltameter, and due to the oxygen and hydrogen clinging to the two platinum plates, suggested to Grove the possibility of prolonging this current by supplying a sufficient quantity of the two gases in contact with platinum. The polarization current soon exhausts the films of oxygen and hydrogen on the two respective plates. By extending the strips of platinum so that they are partly in the liquid and partly in the gas of each tube of the voltameter supplied with water acidulated with sulphuric acid, density 1.2, Grove succeeded in producing continuous currents of sufficient intensity to decompose water and to produce a brilliant spark in broad daylight between two carbon

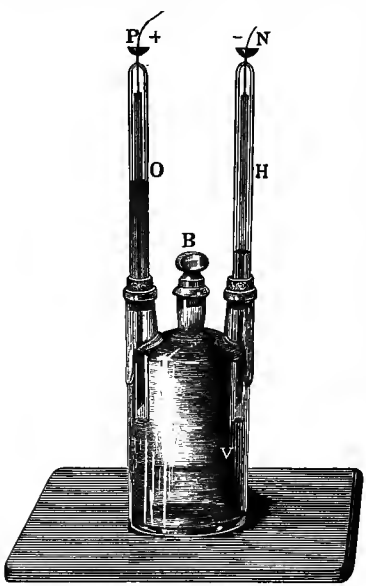


Fig. 52. — Grove's Gas Battery.

points. For this latter purpose he employed fifty pairs.

The figure exhibits the form of gas battery preferred by Grove. *V* is a three-necked Woulff's bottle. In the two outer holes are fitted two glass tubes by means of rubber stoppers. Each tube is open below and contains a piece of platinum foil ending above in a platinum wire, which is sealed into the top of the tube. The entire apparatus is filled with acidulated water through the middle opening *B*, and a current is then passed through till one tube *H* is filled with hydrogen, and the other half-filled with oxygen. If now the battery is removed, and the terminals at *P* and *N* are connected by a conducting circuit, a current flows from the oxygen tube to the hydrogen through the external circuit.

In order to increase the surface of the liquid in contact with the platinum and exposed to the gas, Grove covered the foil with pulverulent platinum by Smee's method of electrolytic deposit. The liquid then rises along the roughened surface by capillary action.

The hydrogen in this cell plays the part of the zinc in a voltaic element. The current through the cell is from the hydrogen to the oxygen — the reverse of the decomposing or charging current.

In modern nomenclature this is a storage battery. The effect of the charging current is to decompose sulphuric acid primarily and water as a secondary reaction; and the accumulation of the products of the electrolysis in the two tubes is a storage of potential energy. When this potential energy is converted into the kinetic energy of a current, all the processes are reversed, the current with the others. In the same way, when energy is stored in the potential form by lifting a weight from the

earth, the running down of this energy by conversion into the kinetic variety involves a reversal of the motion of the weight.

In the electrolytic process the chain of molecules may be represented as follows: —

$$\overbrace{H_2O} \mid \underbrace{H_2SO_4} \mid \underbrace{H_2SO_4} \mid \overbrace{H_2O}.$$

$$\longleftarrow\!\!\!\!\!\!\longleftarrow$$

After the first step in the electrolysis this becomes —

$$H_2 \mid H_2O \mid H_2SO_4 \mid H_2SO_4 \mid O.$$

The oxygen and hydrogen are now at the two ends of the chain; and, leaving out the water as unessential, the chain of the gas battery may be written —

$$\overbrace{H_2} \mid \underbrace{H_2SO_4} \mid \underbrace{H_2SO_4} \mid \overbrace{O};$$

$$\longrightarrow\!\!\!\!\!\!\longrightarrow$$

and this becomes, after the first exchange of atoms among the molecules —

$$H_2SO_4 \mid H_2SO_4 \mid H_2O.$$

Hydrogen is in both cases transferred in the direction of the current, which is shown by the arrow. In the discharge process the oxygen may equally well be supposed to suffer a transfer in the opposite direction, though it is simpler to conceive of the motion of the hydrogen only. The operations of the electrolytic process are then strictly reversed in the recombining process.

The tubes of the gas battery may be filled with the two gases obtained by any other method than electrolysis, with no difference in the result.

If one tube is filled with hydrogen and the other with acidulated water, a current is still obtained, and hydrogen gradually disappears on closed circuit. Grove showed that the current in this case was due to the oxygen absorbed from the atmosphere.

Similar results were obtained with other gases, notably hydrogen and chlorine; also with one gas and a liquid whenever chemical reaction was possible between the two.

70. Upward's Chlorine Battery. — The electrodes are zinc and carbon, the former immersed in water contained in a porous cup, and the latter in water saturated with chlorine gas. The space between the porous cup and the carbon is filled with broken retort carbon. Each cell contains several zincs and carbons joined together in multiple.

Since the chlorine is both the active exciting agent and the depolarizer, the liquid about the carbon is kept saturated with the gas, which passes into the porous cup by diffusion, while the zinc chloride formed diffuses outward. The cell must be closed air-tight to prevent the escape of chlorine.

Each cell consists of a glazed vessel, with an inlet tube near the bottom and an outlet near the top. A glazed cover, with the requisite provision for the passage through of the two electrodes, closes the cell tightly. The chlorine, made from chloride of lime ($CaOCl_2$), is stored in a glazed earthenware cylinder provided with inlet and exit tubulures. The cells and the reservoirs are connected together in series, the top of the reservoir to the bottom of the first cell; the top of this cell to the bottom of the second; and the top of the second back again to the reservoir. Each cell is further pro-

vided with a draw-off stone tap for removal of the zinc chloride formed in the action of the cell.

The E.M.F. is 2.1 volts and very constant. Large cells have been built by Woodhouse & Rawson for charging storage batteries, and they are said to furnish a current of 150 amperes on short circuit.

71. Powell's Thermo-Electro-Chemical Battery.[1] — Differences of potential have often been observed between two plates of the same metal in a solution of a salt of the same, when one plate is at a higher temperature than the other. Thus two zinc rods in sulphate of zinc are at a different potential if their temperatures are different, the one of higher temperature constituting the positive electrode (negative plate) of a voltaic couple.

This property has been applied to the construction of a thermo-chemical couple with copper plates in copper sulphate solution. A horizontal plate is placed in the bottom of the cell, and a well insulated wire leads out, preferably through a glass tube. Another copper plate, with a copper tube attached to its centre, is suspended so that its under surface touches the surface of the solution. Half-a-dozen small openings at the bottom of the copper tube convert it into a rose burner. Gas is conducted in through the tube, lighted at the openings, and the small flames heat copper wires riveted to the copper plate. The transfer of heat to the plate, and so to the liquid, is thus increased.

Under these conditions, a current flows from the warm to the cold plate through the external circuit, and copper is transferred from the cold plate to the warm one through the solution. In other words, the cold plate performs the same function as the zinc in a simple

[1] London Electrical Review, Vol. XX. p. 2.

voltaic element.[1] The energy concerned in the transfer comes from the heat applied. The combination is thus both a primary (heat) battery and an electrolytic cell. The potential energy transformed is in this case represented by the illuminating gas.

The E.M.F. is small, only about 0.035 of a volt with a difference of temperature of 50° C. between the upper and the lower plates.

A small addition of sulphuric acid, which is of utility in an electrolytic cell for copper sulphate, reduces the E.M.F. of the thermo-chemical battery to zero. Copper nitrate may be used in place of the sulphate.

NOTE. — The inventor of this battery describes it with the current flowing through the cell from the warm plate to the cold one, and says expressly that copper is transferred from the top to the bottom (Electrical Review, Vol. XX. p. 2, London). But if the reader will consult the next chapter, he will find an account of tests on this point, with a table of E.M.F.'s at different temperature differences.

72. A Battery Absorbing Oxygen from the Air.[2] — When copper is alternately exposed to the air and immersed in an aqueous solution of ammonia, it oxidizes, and the oxide dissolves as a blue solution of ammoniacal cupric oxide. If the copper remains immersed in the solution at a considerable depth, the supply of oxygen that can reach the copper plate is very limited, and cuprous oxide is formed and dissolved.

If now an aërating plate of platinum foil or platinum sponge is supported on the liquid surface, and connected by a wire with the copper, a current flows through the liquid and the wire, and the process of oxidation and solution is greatly hastened. The platinum plate or

[1] See Chapter IX.

[2] Proceedings Royal Society, Vol. XLIV. p. 182.

sponge condenses oxygen, which is gradually transferred to the copper.

The current rapidly runs down if its density is more than one micro-ampere (millionth of an ampere) per square centimetre of the aërating plate. The E.M.F. may be from 0.5 to 0.6 of a volt. The addition of common salt or of sal-ammoniac reduces the internal resistance and increases the E.M.F.

With a thin layer of spongy platinum as the aërating plate the E.M.F. may be as high as 0.8 of a volt.

Similarly, if a platinum plate is immersed in a solution of ferrous sulphate or sulphurous acid, and an aërating plate is placed on the surface of some dilute sulphuric acid in another vessel; and if the two vessels are connected with a siphon or a piece of moistened candle wick, and the two plates are joined by an electric conductor, the oxygen condensed by the aërating plate will be transferred to the oxidizable solution in the other vessel, with the formation of ferric sulphate or sulphuric acid, and at the same time a current will flow through the circuit.

73. Minchin's Seleno-Aluminum Cell. — Professor Minchin [1] constructs a cell sensitive to light in the following manner: Two small clean plates of aluminum are taken, and a thin layer of sensitive selenium is spread over one of them. Fine platinum wires are then attached to both plates, and they are immersed in presence of each other in a small glass cell containing acetone. Alcohol — preferably methylic — answers very well, except that in a few days the plates become covered with a gelatinous deposit of aluminate of alcohol.

The selenium must be treated by heating and care-

[1] Philosophical Magazine, Vol. XXXI. p. 207.

fully keeping it near the melting-point for some time, till it assumes a very dark brown color. It has then its most sensitive surface.

When a cell, constructed as described, is exposed to light, an E.M.F. is at once developed, and the sensitive seleno-aluminum plate is negative towards the insensitive one, *i.e.* as copper to zinc.

This photo-electric cell is sensitive to all parts of the spectrum, with a maximum in the yellow near the border of the green. The variation in sensitiveness throughout the entire visible spectrum is about 30 per cent.

74. Shelford Bidwell's Dry Battery. — This cell, which grew out of an investigation into the sensitiveness of selenium to light, has thus far only a scientific interest.

On a plate of clean copper is spread a layer of copper sulphide. The sulphide is then compressed in a vise between the copper plate and one of polished steel. The steel plate is next carefully removed, and a thin layer of silver sulphide is spread over the compressed copper sulphide. Finally, a plate of silver is pressed down upon the sulphide and the cell is complete.

The copper plate constitutes the positive electrode, the current flowing through the cell from the silver to the copper. The chemical action consists in the reduction of the sulphide of copper with deposition of copper on the copper plate, and the simultaneous formation of an equivalent amount of the sulphide of silver.

The cell is entirely analogous to the Daniell, with copper and silver in their sulphides in place of copper and zinc in their sulphates.

With copper and silver separated by copper sulphide only no current was obtained; but when free sulphur was mixed with the sulphide, the cell became active.

75. Jablochkoff's Battery. — Carbon is attacked by nitrates in a state of igneous fusion, while iron is not. Hence a vessel of cast iron, cylindrical in form and filled with fused nitrate of potassium or sodium, serves at the same time as a receptacle and as an unattacked electrode. An iron wire helix serves to hold the coke and to conduct to the external circuit. If the nitrate is maintained in a state of fusion, the cell will have an E.M.F. of from one to two volts.

It has been observed that if an aqueous solution of the salt is used instead of the fused nitrate, the poles are reversed, or the iron is the negative electrode and acts like zinc in a simple cell.

76. Battery with Two Carbon Electrodes. — This was devised by Tommasi and Radiguet in 1884. At the centre of a cylindrical glass jar is placed a carbon rod, covered with a thick layer of peroxide of lead, the whole enclosed in a linen bag.

This enclosed electrode is placed in a carbon tube pierced with holes; the two electrodes are then put into the glass jar and filled around with fragments of retort carbon, and a concentrated solution of chloride of sodium added to chloride of calcium. This latter salt serves to retard very much the evaporation of the water.

The carbon rod with the coating of lead peroxide is the positive electrode.

The E.M.F. is from 0.6 to 0.7 of a volt. No action takes place on open circuit, but since polarization sets in rapidly on closed circuit, the cell can be used only for applications requiring an intermittent current. For such purposes it has a very long life. Some of these cells, after remaining in service for several years, operate absolutely as well as the first day they were set up.

CHAPTER IX.

BATTERY TESTS.

77. What a Systematic Test Includes. — The most obvious quantities to be measured are the E.M.F. and internal resistance. While a high E.M.F. is desirable for most purposes, a low E.M.F. is no indication that a battery may not be admirably adapted to its intended work. So low internal resistance is a commendable feature, because, **cæteris paribus**, low internal resistance means high efficiency; but if a battery is to be used on a circuit of high resistance, its own resistance is relatively of less account. For large currents, low internal resistance is a necessity.

It is further very desirable to know the rate, progress, and total amount of polarization that takes place when a cell is kept on a closed circuit of known resistance for a definite period. The results of a test to determine such data respecting polarization can all be expressed graphically in the form of a curve.

So also the promptness and extent of the recovery from polarization are equally essential objects of investigation, and the results can be expressed in the same manner as the polarization.

These data, together with the potential difference at the terminals or electrodes, when the battery is on closed circuit, furnish all that is needed to compute the internal resistance and the current.

An efficiency test can be made only by working a battery to exhaustion. This is not practicable for one of relatively large internal resistance and rapid polarization. For open circuit cells many plans have been devised to secure continuous intermittent test service extending over long periods. But none of these is so satisfactory as to place a battery in actual service and wait for results.

Another important object of inquiry is the amount of depreciation and local action taking place on prolonged standing on open circuit. This is applicable strictly to open circuit cells only.

The practised eye of the observer with experience will not overlook many details of mechanical construction, which are as important to the satisfactory working of a battery as its electrical features.

78. Theory of the Method of Measuring E.M.F. and Internal Resistance. — The E.M.F. is measured by comparing it with that of some standard which is known. The standard employed in the following tests was the author's form of the Latimer Clark cell, having an E.M.F. of 1.44 true volts, or 1.444 legal volts, at 15° C. For ordinary battery tests a rapid method of comparison, accurate to one-half per cent, is all that is required. The condenser method is the only one that admits of sufficient rapidity, and it possesses the required accuracy. For this purpose, a standard mica condenser, divided into fractions so as to admit of using from 0.05 to one microfarad, and a sensitive reflecting galvanometer of from 5000 to 7000 ohms resistance, are required. Also the proper charge and discharge keys, and an ordinary circuit-closer.

The condenser is then charged with the standard cell

and discharged through the galvanometer, and the deflection noted. The same process is repeated with the cell to be tested. The ratio of the deflections produced is the ratio of the electromotive forces of the standard and the cell in question; for the deflections are at least approximately proportional to the quantities of electricity discharged through the galvanometer, so long as those deflections are not large and not widely different; and the quantities are proportional to the electromotive forces charging the condenser, the capacity of which remains constant.

To obtain the internal resistance, we must know the total E.M.F. of the cell, and the difference of potential between its terminals when the circuit is closed through a known external resistance. If, now, it is assumed that the potential difference at the terminals can be measured so soon after closing the circuit that no polarization has set in, then the total E.M.F., previously measured, is the whole fall of potential over the resistance of the entire circuit, while the difference of potential at the battery terminals represents the fall over the known external resistance, which must contain no source of E.M.F. If, therefore, E and E' represent total E.M.F. and terminal potential difference, r and R the internal and external resistance respectively, then —

$$E : E' :: r + R : R.$$

Hence

$$E - E' : E' :: r : R,$$

and

$$r = R\frac{E - E'}{E'}.$$

Since R is known, and E and E' have been measured, r is also known for the given conditions of external resistance and current.

There is reason to believe that the resistance, and probably the electromotive force, of a battery depends to a certain extent upon the current flowing through the battery, and upon the rate of diffusion of the products of the chemical changes taking place. The resistance, and generally the electromotive force, varies also with the temperature of the battery.

All that can be positively affirmed of the value r, obtained as described, is that it satisfies the equation

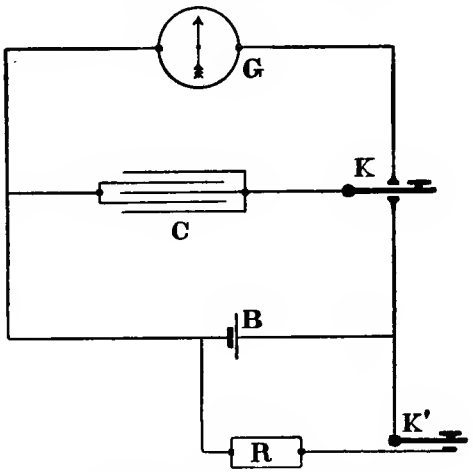


Fig. 53. — Diagram of Battery Tests.

expressing the relation between R, E, and E'. Still, it is true that for widely different values of R, the value of r ascertained by this process will enable us to compute with considerable accuracy the potential difference E' at the terminals available to produce a current through a known external resistance R.

In Fig. 53 are shown diagrammatically the connections of the apparatus for making the measurements

described. The condenser is at C, the galvanometer at G, the battery at B, and the charge and discharge key at K. When the key makes contact with the upper point, the battery is disconnected, and the condenser is in the discharge relation to the galvanometer. When the key K is depressed, the galvanometer is cut off from one side of the condenser, the battery charges the condenser, and as soon as the key again makes contact with the upper point, the condenser discharges through the galvanometer. This operation requires only a fraction of a second. It is repeated several times, first with the standard cell, and then with the battery to be tested.

To measure the internal resistance, the battery is closed by the key K' through a suitable resistance R, which must be known. The key K' should be closed only long enough to charge and discharge the condenser by means of key K. A little practice will enable the experimenter to accomplish this within a second, provided he is supplied with suitable keys. It would not be difficult to have these operations performed mechanically.

79. To Obtain Data for Curves of Polarization, Recovery, Internal Resistance, and Current. — For initial electromotive force and internal resistance, proceed as described in the last section. Then close key K' and at the end of two minutes charge and discharge the condenser to obtain potential difference between the terminals. At the end of four minutes open key K' long enough to quickly and expertly charge and discharge the condenser. This may be so quickly accomplished that there will be no appreciable recovery of the battery from polarization.

If the galvanometer needle can be brought to rest in

two minutes, these operations are repeated alternately every two minutes for an hour. The key K' is then opened permanently, and the total E.M.F. is measured every two or four minutes for an hour longer to follow the recovery from polarization. If practicable, the operations may be repeated at shorter intervals at the beginning of both the polarization and the recovery, when the rate of change of electromotive force is the greatest.

With accurately ruled square paper, the electromotive forces may then be read off by means of a single straight line, which is drawn on the paper as follows: —

Let the vertical lines or ordinates represent electromotive forces, and the horizontal ones the deflections of the galvanometer. Since the E.M.F. is zero if the deflection is zero, the origin is one point of the required line.

Then if the E.M.F. of the standard cell is 1.44 volts, and the corresponding deflection obtained by charging the condenser with it is D; and if d is the deflection corresponding to an electromotive force E to be found, then —

$$1.44 : E :: D : d,$$

and

$$E = 1.44 \frac{d}{D}.$$

It is evident that the relation between E and d is the equation of a right line, and the constant of the equation is $1.44/D$. Assume any value of d, as 100; the corresponding value of E is $144/D$. Lay off this value of E as an ordinate corresponding to an abscissa of 100, and a second point is obtained. The straight line drawn through this last point and the origin is the one required. Then for any other deflection of the galva-

nometer, find the vertical line passing through the number on the axis of abscissas, and follow this line up to its intersection with the straight line just drawn. The number on the horizontal line passing through this intersection, at the point where it meets the axis of ordinates, is the E.M.F. sought. In other words, we have only to find by means of the oblique straight line the ordinate corresponding to any abscissa which represents a deflection.

If the square paper is divided into small sections, each small space may represent a hundredth of a volt. The horizontal scale of deflections may be chosen in any convenient manner.

To find the curve of internal resistance, it is necessary to plot first the curves of polarization and terminal potential difference, with the times of observation as abscissas. Then the short vertical lines between the two electromotive force curves represent the loss of potential, $E - E'$, in the battery itself. Substituting in the formula for r of the last section, the series of internal resistances for the entire time of the test is obtained.

For the current curve, divide the terminal potential differences at the successive times of observation by the constant external resistance R. These quotients, laid off as ordinates, will give the points of the curve.

80. Test of a Typical Leclanché Cell. — The entire data of such a test as has been described are contained in the table. The column headed t gives the time in minutes from the beginning of the test, when the circuit was closed; d and d' are the deflections observed when the condenser was charged, first with the battery circuit open, and then closed through 5 ohms; E and E'

CLOSED LECLANCHÉ CELL.

EXTERNAL RESISTANCE = 5 OHMS.

STANDARD CELL-DEFLECTION, 186. POLARIZATION. RECOVERY.

t	d	d'	E	E'	C	r	t	d	d'	E	E'	C	r	t	d	E
0	214	155	1.661	1.202	0.240	1.90	32	146.5	—	1.136	—	—	—	62	162	1.257
2	—	130	—	1.009	0.202	1.40	4	—	123	—	0.954	0.191	0.95	6	166	1.288
4	156	—	1.211	—	—	—	6	146	—	1.132	—	—	—	70	171	1.327
6	—	128	—	0.993	0.199	1.22	8	—	122.2	—	0.948	0.190	0.92	4	173	1.342
8	155	—	1.202	—	—	—	40	144	—	1.117	—	—	—	8	174	1.350
10	—	127	—	0.985	0.197	1.23	2	—	122	—	0.947	0.189	0.88	82	175	1.358
2	155	—	1.202	—	—	—	4	143	—	1.110	—	—	—	6	176	1.366
4	—	126	—	0.978	0.196	1.11	6	—	121	—	0.939	0.188	0.87	90	177	1.373
6	154	—	1.195	—	—	—	8	143	—	1.110	—	—	—	4	178	1.381
8	—	125	—	0.970	0.194	1.09	50	—	120	—	0.931	0.186	0.87	8	179	1.389
20	152	—	1.179	—	—	—	2	142	—	1.102	—	—	—	102	179	1.389
2	—	124.5	—	0.966	0.193	1.04	4	—	120	—	0.931	0.186	0.88	6	179.5	1.393
4	149.5	—	1.160	—	—	—	6	140.5	—	1.090	—	—	—	110	179.5	1.393
6	—	124	—	0.962	0.192	1.02	8	—	120	—	0.931	0.186	0.88	4	180	1.397
8	148	—	1.148	—	—	—	60	140	—	1.086	—	—	—	8	180.5	1.401
30	—	123	—	0.954	0.191	0.99	—	—	—	—	—	—	—	120	180.7	1.403

have the significations already given to them; while C and r are current in amperes and internal resistance in ohms respectively. The E.M.F. of the standard was 1.443 legal volts.

The same results are expressed graphically in the curves of Fig. 54, all of them being drawn to the same scale, except the internal resistance as indicated.

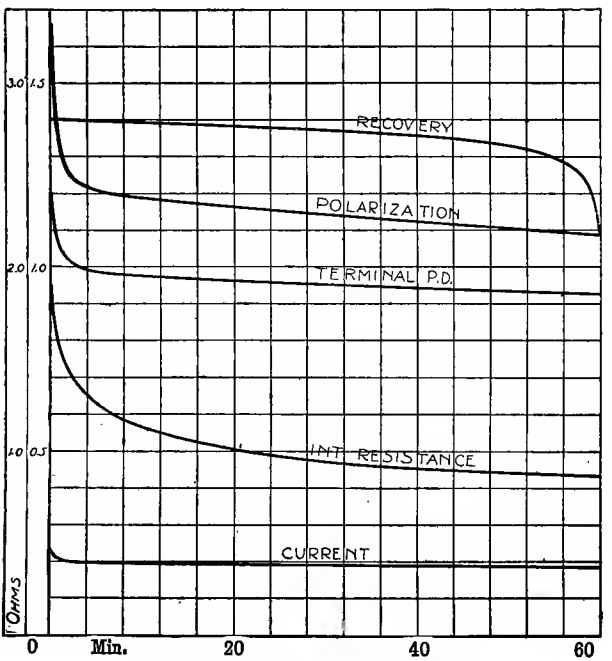


Fig. 54. — Test of Leclanché Cell.

The polarization curve shows a very rapid fall of electromotive force for the first four minutes, and quite a steady decrease up to three-quarters of an hour. The recovery curve shows an almost equally rapid rise of

electromotive force for the first four minutes after opening the circuit. It continues to increase up to the end of the hour, when it is still a quarter of a volt below its initial value. The recovery curve is plotted back from the end of the polarization curve toward the left, so as to exhibit more plainly the depression of the voltage at the end of the two hours test.

The terminal difference of potential is more nearly constant in value after the first steep incline than the total E.M.F.; and the shortening of the intercepts between the two curves shows the decrease in the internal resistance during the hour.

The current after the first two minutes exhibits great steadiness for an open circuit battery. The fall to the end of the hour is only 0.016 ampere, or a little less than 8 per cent.

The initial resistance of this particular cell is high, but it falls more than 50 per cent during the hour. Other individual cells made at the same factory show an internal resistance as low initially as 0.8 of an ohm.

81. Test of Leclanché Cell with Depolarizer Enclosed in Carbon Cylinder. — In cells of this character the depolarizer is not favorably located to accomplish its purpose, since the current leaves the outside of the carbon cylinder rather than the inside where the manganese dioxide is placed. It is exceedingly doubtful if the depolarizer is of much value in this relation to the carbon surface unless it is a soluble salt and diffuses through the liquid.

The large area of carbon surface is an offset, however, to the unfavorable location of the manganese dioxide. A large carbon surface diminishes polarization. It has been found as a result of many experiments that reduc-

tion of zinc surface does not exercise so notable an effect on the current strength as the reduction of carbon surface. Hence the practice of employing zinc rods of small surface area, and carbon plates, rods, and cylinders of much greater superficies.

Attention is called to the slower rate of polarization of this cell, Fig. 55, as compared with Fig. 54, on first

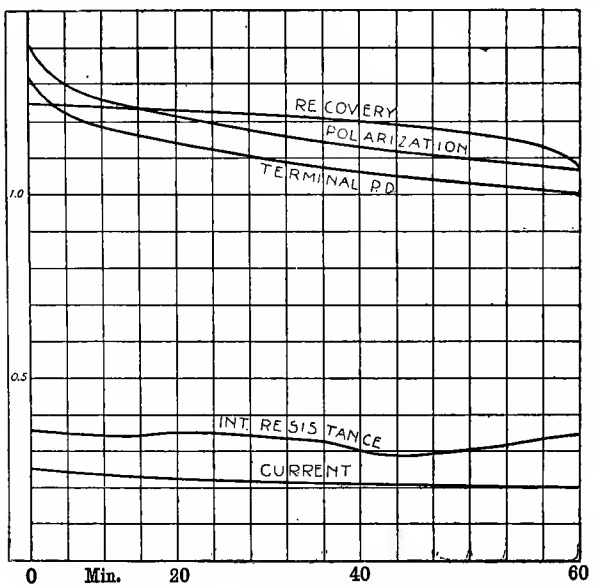


Fig. 55. — Test of Cell with Carbon Cylinder.

closing the circuit. The polarization is more continuous, but not so precipitate. The recovery is of the same character. This feature in the polarization curve, which may be called the "characteristic" of a battery, is advantageous in cells which are designed for service requiring ordinarily the closing of the circuit for only

a few seconds intermittently. The polarization is less for short intervals than with cells having a steeper polarization curve at the beginning.

The terminal potential curve runs nearly parallel with the total E.M.F. curve, and the vertical intercepts between the two are short. With 5 ohms external

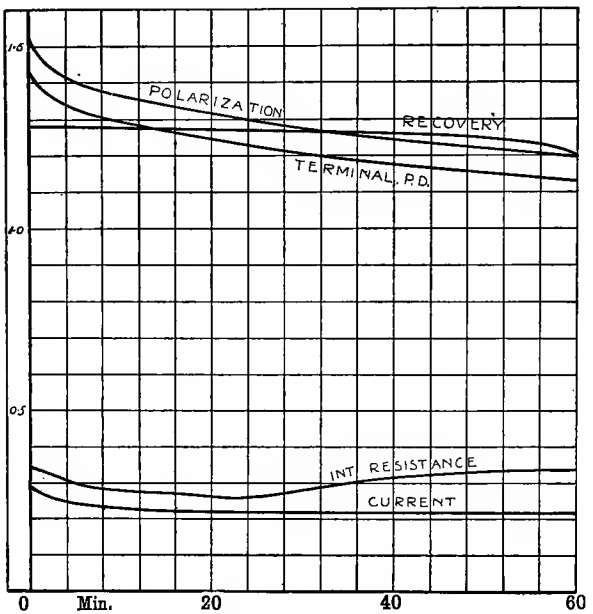


Fig. 56.—Test of Another Carbon Cylinder Cell.

resistance, the uniform value of R for all these curves, unless another value is given, the internal loss of energy in this cell is only 6.2 per cent, the internal resistance averaging about 0.33 of an ohm. The current fell from 0.26 to 0.2 of an ampere during the entire hour.

Fig. 56 illustrates another cell of the same general

characteristics, but of a different manufacture and smaller zinc surface. Both have the black oxide of manganese enclosed in a carbon cylinder, and both show polarization and recovery curves of the same character, though the recovery of the latter is less marked. It has a higher E.M.F. and a slightly smaller internal resistance. The energy wasted internally averages about 5.7 per cent.

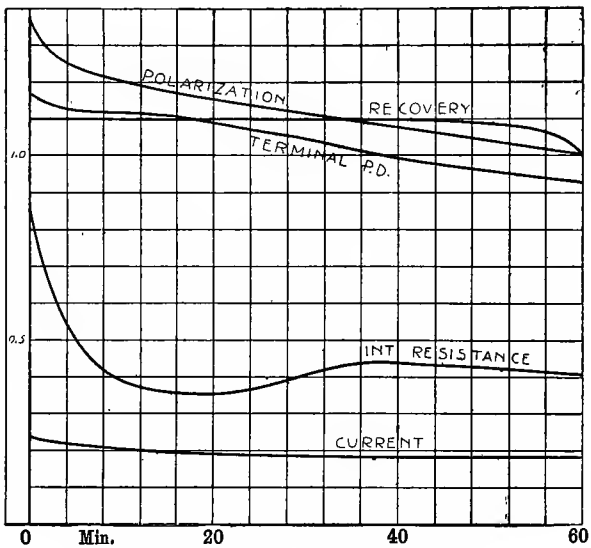


Fig. 57. — Zinc-Carbon Cell without Depolarizer.

It is to be borne in mind that these particular values are derived from individual cells, and do not represent the average obtained from a number of the same type.

82. Test of Zinc-Carbon Cell without Depolarizer. — The curves of Fig. 57 are derived from an investigation of a well-known type of battery employing ammonic chloride, but no depolarizer whatever. The polarization is some-

what more pronounced at the start, but has the same progressive character as in the two preceding cases.

The internal resistance exhibits marked irregularities, and is higher than would be anticipated, considering the extent of carbon surface. The current is nevertheless quite regular and has a mean value somewhat above 0.2 of an ampere.

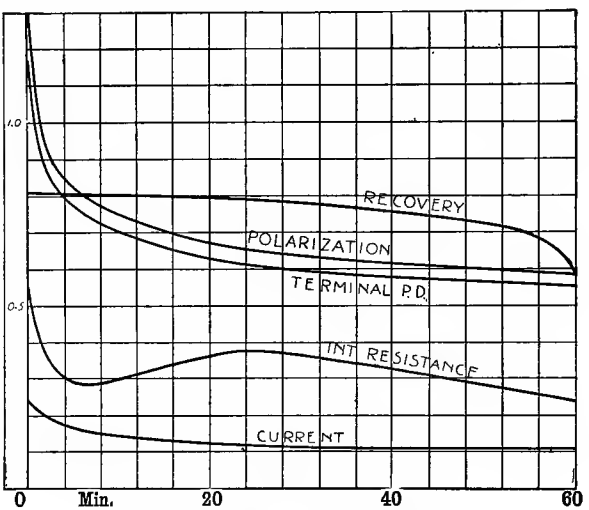


Fig. 58. — Curves from a Dry Cell.

83. Test of a "Dry" Cell. — A dry cell has the excitant in the form of a semi-fluid or porous, pasty mass. In so far as polarization depends upon diffusion the dry cell may be expected to show a more marked and persistent depression of voltage when placed on an external resistance of no more than 5 ohms. Such anticipations are abundantly justified by the curves of Fig. 58, derived from a test of one of the best known cells of this class. The E.M.F. fell to less than one-half its initial value in

the hour, and its recovery during the following hour was quite leisurely. The semi-liquid electrolyte admits of only slow diffusion, even though ingredients may be added to make the mass porous. The internal resistance of this cell was not large, but was irregular, and the current fell during the test to less than half its initial value, because of the great drop in potential.

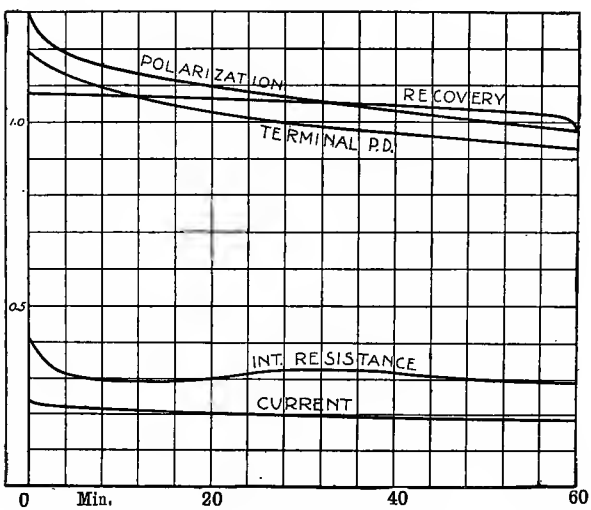


Fig. 59. — Second Dry Cell.

Another type of dry cell, not described in the preceding pages, furnished the curves of Fig. 59. It must be admitted that this cell makes a showing comparing favorably with zinc-carbon cells set up with a liquid electrolyte.

The polarization is leisurely, the internal resistance only three-tenths of an ohm, and the current averages fully 0.2 of an ampere.

Two of these same cells were subjected to a test in which for four months continuously they actuated a relay-sounder of about 100 ohms resistance every second, by means of a seconds-pendulum. They showed no perceptible deterioration in that time, though on two or three occasions the clock was stopped for several hours, during which time the circuit remained closed. On

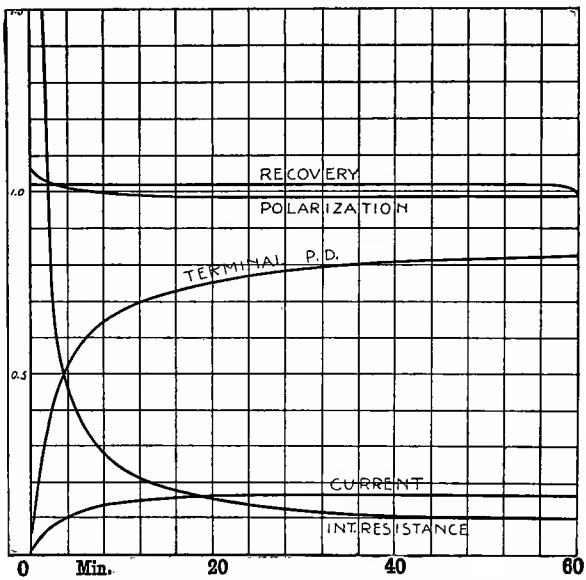


Fig. 60. — Curves from Chloride of Silver Cell.

starting the clock, the relay-sounder again operated without readjustment. After standing idle for seven months these same cells were again put to the same service in time measurements, and they are still as efficient as ever after three months' additional use.

84. Test of a Silver Chloride Cell. — The curves (Fig. 60) obtained from a small silver chloride cell, made by

the author, serve to illustrate a number of points. The chloride was cast in a carbon mould on a silver wire, leaving a very small surface of silver exposed to the exciting liquid, which was dilute ammonic chloride.

The internal resistance on first closing the circuit, before any metallic silver had been reduced from the chloride, was 79.7 ohms. It fell during the hour to one ohm, the scale of the resistance curve being one-tenth as large as that of the others. This precipitate fall of resistance is due to the reduction of silver from the chloride, which converts a poor conductor into the best one known.

Coincident with this fall of internal resistance is the rise of potential difference at the terminals and of the current. The latter does not rise above 0.17 of an ampere. The cell was a small one, with about two square inches of zinc surface. The polarization of the silver chloride cell is so slight as to justify its inclusion in the list of constant current batteries; for the E.M.F. is nearly constant, and the drop in internal resistance causes the current to increase in intensity instead of the reverse. The recovery from polarization is extremely prompt, and occurs within the first two or three minutes after opening the circuit. The initial value of the E.M.F. is not regained, but the final loss is less than 0.05 of a volt.

85. Efficiency Test of Copper Oxide Battery. — An efficiency test consists of two parts: —

First, the determination of the total quantity of electricity obtained by the consumption of a definite weight of zinc, compared with the quantity of electricity required to deposit the same weight in electrolysis.

Second, a comparison of the useful energy in the

external circuit with the internal energy as heat waste in the cell itself.

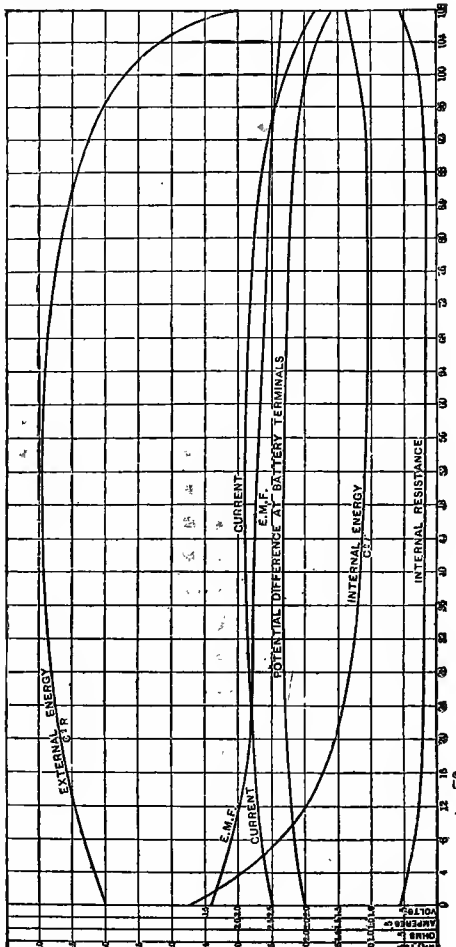


Fig. 61. — Test of Edison Copper Oxide Cell.

For the first, the zinc must be weighed at the beginning and end of the test, and the whole number of ampere-

hours must be determined. This gives the quantity of electricity obtained by the consumption of a known weight of zinc. The quantity required to deposit the same weight of the metal can be calculated from the electrochemical equivalent of zinc.

For the second part of the test, the internal resistance must also be measured at intervals during the run. Then the energy lost as heat in any circuit of resistance r is C^2r; for energy is the product of current and electromotive force, and by Ohm's law electromotive force is Cr. Hence energy is C^2r. The external resistance being known also, the external energy is calculated in the same way.

The curves of Fig. 61 express graphically the results of such a test made with great care by Mr. A. E. Kennelly in the Edison laboratory. Four 300-ampere-hour cells were taken at random from the stock. They were joined in series in a circuit of 0.8 of an ohm external resistance. The total run was 108 hours. The external energy increased quite up to the middle of the time, because of the continuous reduction in internal resistance.

The following are details of the computation: —

Weight of zinc before test	10,017 gms.
" " " after "	8,567 "
Total loss	1,450 "
Loss calculated from output . . .	1,444 "
Loss by local action	6 "

Mean current	2.76 amperes
" E.M.F.	2.8 volts
Total quantity in ampere-hours . .	298

The ampere-hours are the product of the mean current and the time, or $2.76 \times 108 = 298$.

Taking the electrochemical equivalent of zinc as 0.0003367, the calculated loss is as follows: —

$$298 \times 3600 \times 0.0003367 = 361 \text{ gms. per cell.}$$
$$361 \times 4 = 1444 \text{ gms. for 4 cells.}$$

The quantity 0.0003367 is the weight in grammes deposited by one coulomb, — an ampere for one second. Hence ampere-hours must be multiplied by 3600 to reduce to ampere-seconds or coulombs.

In reading the figures at the left of the diagram, all except those relating to current must be divided by 4 to reduce to the values for a single cell.

An efficiency test of this same type of cell, conducted by the author, showed curves approximating much more closely to straight lines than those of the diagram. The E.M.F., current, and internal resistance were even more constant after the first few hours than those represented above. The total output for a single cell was 390 ampere-hours.

A 15-ampere-hour cell tested to exhaustion gave 10.1 ampere-hours and 7.5 per cent loss of zinc by local action. This cell had been standing a long time with the undissolved alkali exposed to the air.

86. Testing Battery Designed for Small Lamps. — The following method for testing primary batteries, designed for lighting small incandescent lamps, is recommended by Mr. I. Probert.

It may be impracticable to measure exactly the current flowing by the direct use of the ammeter, as the resistance of the latter, though low, is usually sufficient to materially reduce the current when the instrument is

inserted in the circuit. The present method is said to overcome this difficulty entirely. The illustration shows the connections.

The battery *B* to be tested is joined up to the lamp (which has a voltmeter *V* across its terminals), the switch *S* being turned to the position shown. Under these conditions the battery works directly on the lamp, and the voltmeter *V* gives the voltage between the lamp terminals. In order to determine the current, the switch *S* is turned to the position shown by the dotted

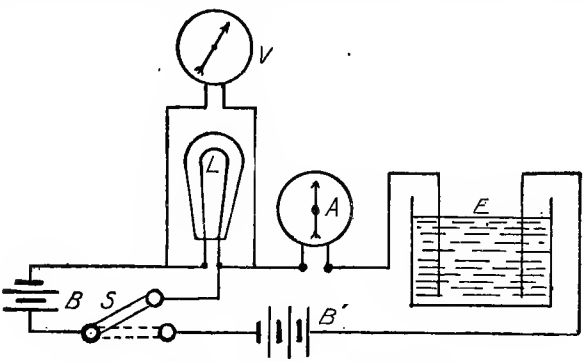


Fig. 62. — Testing Battery for Current.

lines; this brings into circuit the auxiliary battery (preferably small portable accumulators, as they have a low resistance), the ammeter *A*, and the electrolytic resistance *E*. The current from *B*, though reduced by the resistance of the ammeter, is reinforced by the auxiliary battery *B'*; and by adjusting the distance between the plates of the electrolytic resistance the current can be adjusted to the greatest nicety, until the deflection of *V* is the same as it was previous to the turning of the switch *S*. Hence the ammeter *A* now shows the

current which, under the former conditions, was flowing through B. The observation being taken on A, the switch S is turned back to the position shown in the figure, and the battery B continues to work under the practical conditions.

87. Analysis of the Temperature Coefficient of a Battery. — If the temperature coefficient is a purely thermo-electric effect, then it should be susceptible of analysis by a measurement of the thermo-electric power of the two metal-liquid pairs. If, for example, the thermo-electric power of zinc—zinc sulphate and copper—copper sulphate can be measured separately, then their algebraic difference should represent the temperature coefficient of the Daniell cell, except so far as it may depend upon the thermo-electric power of the liquid pair, zinc sulphate—copper sulphate, which is the only other contact of dissimilar substances in the cell.

So, also, if we combine the results obtained by measuring the thermo-electromotive force of zinc—zinc sulphate and mercury—mercurous sulphate in zinc sulphate, the result should be the temperature coefficient of a Clark standard cell.

The meaning of thermo-electric power may perhaps be explained with advantage. If two junctions are at two temperatures $t°_1$ and $t°_2$, of which

$$t° = \frac{t_1 + t_2}{2}$$

is the mean; and if E is the E.M.F. of the pair under these conditions, then

$$\textit{The thermo-electric power at } t° = \frac{E}{t_2 - t_1}.$$

88. To Determine the Thermo-Electric Power of Zinc—Zinc Sulphate. — For this determination it is necessary

to have two contacts of zinc and a solution of its sulphate so related that one can be kept at a constant temperature, while the other is brought to successive different temperatures. Two stout glass tubes, about four inches (10 cm.) long and three-quarters of an inch in diameter, were connected near the tops by a narrow glass tube 10 inches (25 cm.) long. This will be called the "experimental cell." It was filled with zinc sulphate solution saturated at zero, and two zinc wires about a foot in length were suspended so as to dip half

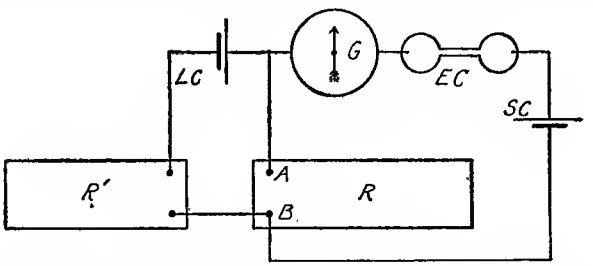


Fig. 63. — Diagram Showing Method of Measuring Thermo-Electric Power.

or three-quarters of an inch into the liquid. The immersed ends were slightly amalgamated. Two thermometers were hung from a convenient support so that their bulbs dipped into the solution at the same depth as the zinc wires. The liquid filling the small tube served to make the electrical connection between the two limbs.

The electromotive force was measured by the following method: R and R' in Fig. 63 are two resistance boxes of 10,000 ohms each. For most purposes R' may be less than 10,000. They must be of the most exact adjustment, or the errors, if any, must be known. They are connected in series with a good Leclanché cell of

higher E.M.F. than a standard Clark cell. Two Daniell cells would perhaps answer as well, but they are not so convenient.

The total resistance in the circuit must be kept at 10,000 ohms, partly in R, and the remainder in R'. In a derived circuit from AB, the terminals of R, are placed in series a Clark cell SC, the experimental cell EC, and the long coil galvanometer G. It is better to include a resistance of 10,000 or 20,000 ohms besides in this circuit. The standard cell must be so connected that its positive is joined to the same terminal as the positive of the main circuit Leclanché cell LC. A key must be placed in both circuits, preferably a double successive contact key of the style used with a Wheatstone's bridge. The first points coming in contact close the main circuit; increased pressure brings the second pair of contact points together, closing the derived circuit. When the pressure is relieved, the derived circuit opens first, and finally the main circuit.

The adjustment consists in changing the resistance in the two boxes, keeping their sum 10,000, till the closing of the circuit does not cause the galvanometer needle to swing. A balance then subsists between the E.M.F. of SC and the fall of potential in the main circuit over the resistance between A and B. The cell EC is not included in the derived circuit in this first balance. The E.M.F. of the standard cell being known, the fall of potential over a single ohm in the main circuit is then known.

The galvanometer employed was a Thomson reflecting instrument, astatic, and having a resistance of 7000 ohms. A change of a single ohm from R to R', or the reverse, when the balance is nearly effected, is perfectly

evident in the swing of the mirror. In fact, when a balance has been secured, if the key is kept closed for two or three seconds, the polarization of the main circuit Leclanché cell is always evident in the overthrow of the balance.

The next step is to include the experimental cell in the circuit as shown in the figure. Both limbs are surrounded with broken ice, and their temperature is nearly or quite the same. It is usually necessary to change the resistance R by a small number of units, perhaps two or three, in order to restore the balance.

One of the limbs is then heated by successive stages, using a bath of warm water. The temperature is allowed to become as nearly stationary as possible, and a balance is again brought about as before. If the resistance R must be increased to bring the galvanometer needle to zero, then the E.M.F. of the experimental cell is so directed as to place the cell in series with the standard cell. If R must be diminished to secure a balance, the experimental cell EC is in opposition to the standard. The closing of the key therefore indicates at a glance which pole of EC is positive. For if EC is in series with SC, the galvanometer needle will swing in one direction; if in opposition to SC, it will swing in the other direction; and the direction of the swing always indicates to the operator whether R must be increased or diminished to effect a balance.

With zinc in zinc sulphate the heating of one limb always produces an E.M.F. tending to make the zinc in the cold the positive plate, or to produce a current **from cold to hot through the cell.** The zinc in the cold limb acts like the zinc of a simple voltaic couple.

The table gives the data of one series of experiments.

TABLE I.

Temp. C. Left Limb.	Temp. C. Right Limb.	Temp. Difference (corrected).	Resistance in R in Balance.	Change in E.M.F. in Legal Volts.	E.M.F. per Degree C.
0.6	0.4	0.2	9141	...	...
9.8	0.4	9.2	9183	0.00660	0.00072
14.4	0.4	13.8	9199	0.00911 ?	0.00065 ?
19.0	0.4	18.4	9225	0.01319	0.00072
27.8	0.4	27.2	9269	0.02011	0.00074
37.6	0.4	37.0	9320	0.02812	0.00076
47.3	0.4	46.7	9377	0.03707	0.00079

The observation marked doubtful I had reason to think included an error in making the balance.

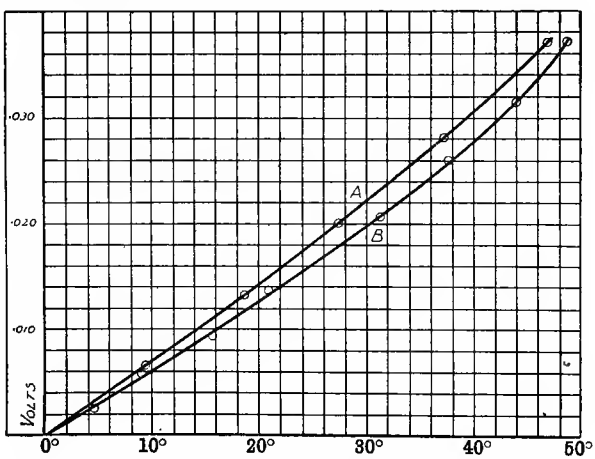


Fig. 64. — Thermo-Electric Power of Zn—$ZnSO_4$ and Cu—$CuSO_4$.

The mean thermo-electric power for a temperature of 23°.85 C. is therefore 0.00079.

89. Thermo-Electric Power of Copper—Copper Sulphate. — The apparatus was set up in precisely the same manner as before, with a solution of chemically pure copper sulphate of density 1.11. Two freshly electroplated copper wires were used as electrodes to dip with the thermometers into the solution. The current produced on heating one limb was found to have the same direction as in the case of zinc sulphate, viz. from the cold limb to the warm through the liquid. The copper in the cold acts like the zinc of a simple voltaic cell. The table following contains all the data.

TABLE II.

Temp. C. Left Limb.	Temp. C. Right Limb.	Temp. Difference (corrected).	Resistance in R to Balance.	Change in E.M.F. in Legal Volts.	E.M.F. per Degree C.
0.6	0.4	0.2	9129	...	...
5.1	0.4	4.5	9145	0.00252	0.00056
9.6	0.4	9.0	9166	0.00582	0.00065
16.1	0.2	15.7	9189	0.00944	0.00060
21.7	0.6	20.9	9216	0.01369	0.00066
32.1	0.5	31.4	9260	0.02061	0.00066
38.4	0.5	37.7	9295	0.02611	0.00069
44.7	0.6	43.9	9330	0.03162	0.00072
49.4	0.6	48.6	9353	0.03524	0.00073

The mean thermo-electric power for the copper—copper sulphate couple is therefore 0.00073 for the mean temperature of 25° C. The results for both zinc and copper immersed in their sulphates are plotted in the curves of Fig. 64, in which curve A refers to zinc and zinc sulphate, and curve B to copper and copper sulphate. The total E.M.F.'s in legal volts, due to heating one limb, are plotted as ordinates, and the differences of

temperature as abscissas. It will be noticed that both are slightly concave upward, indicating an increase of the thermo-electric power with rise of temperature.[1]

90. Application to a Daniell Cell. — Since both zinc and copper, each in a solution of its sulphate, tend to become negative when heated, or to play the rôle of copper in a simple voltaic element, it is evident that they will exhibit the same phenomenon when set up together as a Daniell cell. When the entire cell is heated, the E.M.F. tends to rise because of the effect at the copper side of the couple, while the heating of the zinc and its sulphate gives to the zinc the power of generating a counter E.M.F. Whether or not the E.M.F. of the cell as a whole will rise or fall with rise of temperature depends upon the relative thermo-electric power at the two sides. The thermo-electric power of $Zn—ZnSO_4$ is a little greater than that of $Cu—CuSO_4$, so that the voltage of the cell falls by a very small coefficient per degree rise of temperature. The near equality of the two thermo-electric powers explains the small temperature coefficient of the Daniell cell.

A little consideration will show that if the $Cu—CuSO_4$ side of a Daniell cell alone is heated, the E.M.F. of the cell will increase, while heating of the $Zn—ZnSO_4$ side

[1] Since these experiments were made, the author has ascertained that similar ones were made by Bouty in 1880 (Journal de Physique, 1880, p. 229). Bouty made use of a similar method, but employed a Lippmann voltmeter for electromotive forces. His results are 0.0006947 and 0.0006885 for zinc and copper in their own salts respectively, expressed as fractions of the E.M.F. of a Daniell. If it is assumed that the Daniell had an E.M.F. of 1.08 volts, the results of M. Bouty are 0.00075 for $Zn—ZnSO_4$, and 0.00074 for $Cu—CuSO_4$. Considering the small electromotive forces to be measured and the many disturbing causes, such as oxidation of the surfaces and convection currents, the results are in very good agreement.

alone will cause a somewhat greater decrease of E.M.F. The relative coefficients in the two cases were measured by setting up the experimental cell as a Daniell, making use of the same solutions that were used in the preceding determinations, and inserting in the small connecting tube between the two limbs a plug of purified asbestos to prevent intermixture of the two sulphates. After a balance had been obtained with a Rayleigh standard cell the experimental Daniell was substituted for it. A comparison of the E.M.F. of the two was thus made, and data secured to calculate the changes in the voltage of the Daniell by the subsequent heating. The resistance to balance the Rayleigh cell at 18°.7 C. was 9134 ohms. The E.M.F. of the cell at this temperature is 1.434 legal volts. Hence the fall of potential over one ohm is 0.000157 legal volt. This constant is used to calculate changes in E.M.F. of the Daniell under test.

TABLE III.

Temp. C. $Zn-ZnSO_4$ Limb.	Temp. C. $Cu-CuSO_4$ Limb.	Corrected Temp. Difference.	Resistance in R to Balance.	Change in E.M.F. in Legal Volts.	E.M.F. per Degree C.
1.0	0.9	0.1	6935	...	...
10.8	0.8	9.9	6896	0.00612	0.00062
18.8	0.9	17.8	6864	0.01115	0.00063
29.6	1.2	28.3	6815	0.01884	0.00067
45.9	1.3	47.5	6709	0.03548	0.00075
1.5	1.8	0.3	6948	...	...
1.4	15.2	13.5	6994	0.00722	0.00053
1.4	26.4	24.7	7036	0.01382	0.00056
2.0	38.8	36.5	7087	0.02182	0.00060
1.4	40.0	38.3	7093	0.02277	0.00059
1.3	48.5	47.9	7129	0.02842	0.00061

The foregoing table of results justifies the anticipation respecting the changes in E.M.F.; for it will be observed that heating the zinc end of the experimental cell causes a marked diminution of the E.M.F., while the opposite result follows the heating of the copper end.

The coefficients in this case are both smaller than when each metal in its sulphate was used in both limbs

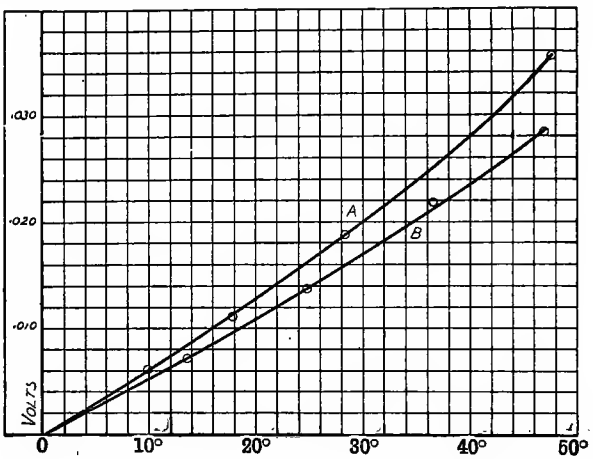


Fig. 65. — Thermo-Electric Powers from Daniell Cell.

of the cell. The difference is small in the case of zinc, but larger in the case of copper. Another series of measurements, made by heating the copper end of the chain, gave almost identical results.

The changes in E.M.F. resulting from heating one limb are positive, and from heating the other, negative. Both are plotted as positive ordinates in the figure in order the better to compare them and exhibit the differences. Curve *A* belongs to zinc, and curve *B* to copper.

91. Temperature Coefficient of a Daniell Cell. — A comparison of the thermo-electric powers of Tables I and II shows that the resultant effect upon a Daniell cell, due to heating the cell as a whole, should be the difference of the two thermo-electric powers, or $0.00079 - 0.00073 = 0.00006$ volt per degree, if the effect of heating the junction of the two sulphate solutions is negligible.

To investigate this last question, an experimental cell was made in which the connecting tube was curved so as to include a long U, and the junction of the two sulphates was at the bottom of this U when the cell was set up as a Daniell. After balancing in the usual manner, the U-tube was placed in a hot water bath, by which its temperature was raised from 17° to 52°, or through a range of 35° C. No effect was produced upon the E.M.F. of the cell; or if any, it was less than one ten-thousandth of a volt for the entire range of 35°.

Many difficulties were encountered in the attempt to determine directly the temperature coefficient. They appear to be due to small changes in the E.M.F., occasioned by oxidation. The expedient was finally resorted to of setting up the experimental cell as a Daniell with amalgamated zinc and oxidized copper wires and allowing the apparatus to stand for fifteen hours. Consistent results were then obtained with both rising and falling temperatures. The whole cell, except the tops of the tubes, was immersed in water. The following data were obtained: —

Resistance to balance at	16°.8	. . . .	6976 ohms
" "	57°.6	. . . .	6956 "
" "	15°.2	. . . .	6975 "

A rise of temperature of 40°.8 caused a diminution of 20 ohms to balance, while a fall of 42°.4 increased the requisite resistance 19 ohms. An independent balance with a standard cell gave the fall of potential over a single ohm as 0.0001561 volt. The mean value of the change in voltage per degree was accordingly 0.000073 of a legal volt. This is in very satisfactory agreement with the result calculated from the separate thermo-electric powers.

The E.M.F. of the experimental cell was 1.09 legal volts. Hence the temperature coefficient is $0.000073 \div 1.09 = 0.000067$. The effect of a change of temperature on the Daniell cell is practically negligible. It is smaller than known disturbances which are assignable to other causes.

92. Thermo-Electric Power of Mercury—Mercurous Sulphate. — Some chemically pure mercury was poured into each branch of the experimental cell, and on this was placed neutral mercurous sulphate free from the mercuric form. Both branches and the thin connecting tube were then filled with a neutral solution of zinc sulphate saturated at 0° C. Connection was made with the mercury in each limb by sealing a long platinum wire into a glass tube, leaving a short portion of the wire exposed at the sealed end. This was pushed down into the mercury on either side.

The cell so set up was then immersed in melting snow and connected in series with the Rayleigh standard, as shown in the diagram, Fig. 63.

By the standard cell the fall of potential over each ohm in R was found to be 0.0001571 of a volt.

One limb of the experimental cell was then heated, while the other was kept at 0° C., with the results shown by the table.

TABLE IV.

Temp. C. Left Limb.	Temp. C. Right Limb.	Temp. Difference.	Resistance in *R.* to Balance.	Total E.M.F. in Legal Volts.	E.M.F. per Degree C.
0°	0°	0°	9150	—	—
8.30	0°	8.30	9161	0.00173	0.00021
14.50	0°	14.50	9170	0.00314	0.00022
20.70	0°	20.70	9179	0.00456	0.00022
26.70	0°	26.70	9288.5	0.00605	0.00023
35.80	0°	35.80	9204	0.00833	0.00023
42.60	0°	42.60	9219 ?	0.01053	0.00025 ?
49.25	0°	49.25	9226	0.01163	0.00024

The observation next to the last is marked doubtful because there was reason to suspect an error independently of the failure of this observation to agree graphically with the others.

In Fig. 66 the results are plotted in the curve *B*, together with those derived from zinc—zinc sulphate. These measurements include, of course, the effect of the contact of the platinum with the mercury, as well as that of $ZnSO_4$ and Hg_2SO_4. But these were purposely included with a view of analyzing the temperature coefficient of the Clark cell.

The direction of the E.M.F. produced by heating the $Hg—Hg_2SO_4$ is such as to produce a current through the cell from the cold to the warm limb, precisely as in the preceding cases.

When therefore a Clark cell is warmed, there is a tendency to make both poles positive. The effect at the mercury or positive electrode is added to the whole

E.M.F. of the cell, while that at the zinc or negative electrode is opposed to the E.M.F. of the cell, as a whole, and must be subtracted. The algebraic result, then, is the difference of the two thermo-electric powers, and is negative because the $Zn—ZnSO_4$ one is numerically larger than the other. The difference is 0.00079 less 0.00024, or 0.00055.

These are the mean values of the thermo-electric powers. If we apply them to the corresponding equa-

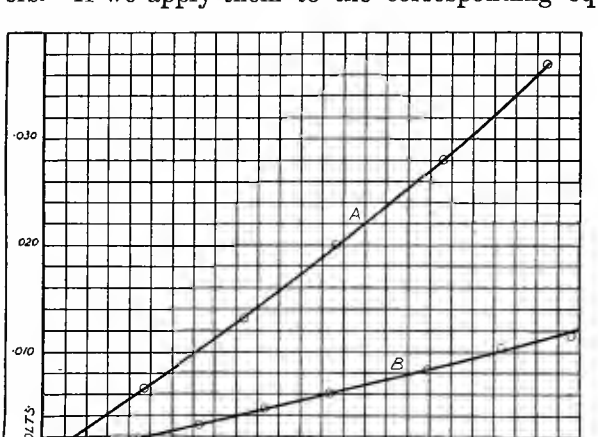


Fig. 66. — Thermo-Electric Power of $Hg—Hg_2SO_4$ and $Zn—ZnSO_4$.

tion for the E.M.F. of a Clark cell, involving only the first power of the temperature, we should write

$$E_t = E\,[1 - x\,(t - 15)],$$

in which x is to be found. In the author's cells, with the solution used above and with the zinc separated from the mercury salt, the E.M.F. is 1.44 true volts at 15° C.

Hence $$E_t = 1.44\,[1 - x\,(t - 15)].$$

If the difference between the thermo-electric powers at the two sides of the cell is the change in volts per degree, then from the preceding equations

$$Ex = 1.44\,x = 0.00055.$$

Whence $$x = 0.000381.$$

Now the thermal coefficient of such a cell is 0.000386 at 15° C. (see section 62). The agreement between the two methods is closer even than one might anticipate.

93. The Experimental Cell as a Clark Cell. — By simply substituting an amalgamated zinc wire, dipping into the zinc sulphate, for the platinum wire of the last experiment, the experimental cell became a Clark standard. Heating up the mercury side alone increased the E.M.F. of the cell; heating the zinc side alone reduced the E.M.F. The results are embodied in the table.

TABLE V.

Temp. C. $Zn + ZnSO_4$.	Temp. C. $Hg + Hg_2SO_4$.	Temp. Difference.	Resistance in R to Balance.	Difference in E.M.F. in Legal Volts.	E.M.F. per Degree C.
15.75	15.8	0.05	9202	—	—
15.80	23.6	7.80	9214	0.00189	0.00024
16.00	34.2	18.20	9232	0.00472	0.00026
16.20	43.2	27.00	9247	0.00708	0.00026
16.25	50.7	34.45	9262	0.00944	0.00027
16.25	15.7	0.55	9207	—	—
23.25	15.7	7.55	9169	0.00598	0.00079
31.60	15.7	15.90	9124.5	0.01298	0.00082
40.00	15.7	24.30	9088	0.01872	0.00077
49.40	15.7	33.70	9029	0.02800	0.00083

The thermo-electric power is in both cases slightly higher than in the experiments on the same metals and their salts separately. But the difference of the mean values is 0.00056 as compared with 0.00055 of the last section. The temperature coefficient of the Clark cell, calculated as before, would be in this case 0.000388. It must be admitted that both of these results differ from the coefficient obtained by the ordinary direct method by a quantity well within the errors of observation.

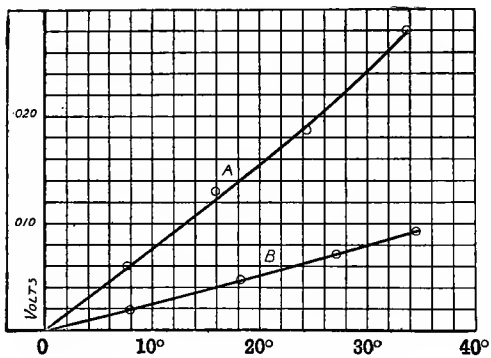


Fig. 67. — Thermo-Electric Power from Clark Cell.

The curve *A* of Fig. 67 shows the effect of heating the zinc end alone of the chain, and curve *B* the mercury end.

All of these curves are slightly concave upward, indicating a small increase of thermo-electric power as the mean temperature increases. Since the mean temperature in this last experiment was 33°, and in the preceding ones on the same metals and metallic salts separately was 24°, the higher values of the thermo-electric power obtained in the present case are partly due to the higher mean temperature.

94. Electromotive Forces of Various Combinations. — A number of questions have arisen in the preceding pages of this book relating to the effect of amalgamation, of concentration of the solutions, of wearing away of zinc at and near the liquid surface, and the like. The experimental cell heretofore described was brought into service for the purpose of determining some of these questions.

1. The experimental cell was set up with zinc sulphate solution, and was supplied with an amalgamated zinc wire in one limb and an unamalgamated one in the other. The amalgamated wire served as the positive plate of a simple cell, or this wire was attacked by the solution more than the other. Zinc then gives a slightly higher E.M.F. when amalgamated.

2. A saturated solution of ammonic chloride was introduced into one limb of the experimental cell, and a 5 per cent solution of the same into the other limb, with amalgamated zinc wires in both.

Resistance to balance Rayleigh cell at 18°.4 . . .	9148
" " with experimental cell in series,	8971
Difference	177

E.M.F. of exp. cell = $177 \times 0.000157 = 0.028$ volt.

The zinc in the dense solution acts like the zinc of a simple voltaic element. The denser the liquid the greater the tendency of zinc to replace the ammonium of sal-ammoniac.

3. The following combination was then tried: —

$$Zn \mid ZnCl_2 \mid NH_4Cl \mid Zn.$$

$$\leftarrow\!\!\!

The result was an E.M.F. producing a current through the cell in the direction of the arrow; or the zinc in the ammonic chloride is the positive plate and negative electrode.

Resistance to balance experimental cell alone . . . 1710
" " Rayleigh cell at 18°.4 . . . 9148
Hence E.M.F. of exp. cell is $1710 \times 0.000157 = 0.268$ volt.

4. The next combination was —

$$Zn \mid ZnCl_2 + NH_4Cl \mid NH_4Cl \mid Zn.$$
$$\longleftarrow\!\!\!

end, on the contrary, caused the E.M.F. to fall. No measurements were made.

6. The ammonic chloride solution was replaced by substituting a solution of $ZnCl_2$, made by adding four parts of water to one of saturated zinc chloride. An oxychloride of zinc formed and was filtered off.

The E.M.F. was 1.01 volts. Heating produced qualitatively the same effects as before.

95. Relative Value of Oxidants in Batteries. — Some interesting and valuable experiments have recently been made by J. T. Sprague, designed to test the relative merits of the more powerful oxidants used in primary batteries. For this purpose he constructed a cell with a small porous vessel, which held 400 fluid grains with the carbon plate, so as to have the conditions exactly the same for each substance. The external circuit contained a large tangent galvanometer, and a copper depositing cell to measure the total work done by the 400 grains of each oxidizing agent.

The following are the measured resistances of the liquids: —

	Sp. gr.	Resist.
1. Sulphuric Acid 1, water 12 vols. . . .	1.085	60.00
2. Sulphate of Copper, saturated	1.172	656.00
3. Potassium Bichromate, sat. sol. . . .	1.048	698.00
4. Same + $\frac{1}{12}$ vol. H_2SO_4	1.139	70.00
5. Sodium Bichromate, sat. sol.	1.422	220.00
6. Same + $\frac{1}{2}$ vol. H_2SO_4	1.552	80.40
7. Chromic Acid, 1000 parts to water 1250,	1.353	48.70
8. Chromic Acid, 2250 grs. + 1 fl. oz. H_2SO_4,	1.454	57.90
9. Nitric Acid	1.375	5.69

These solutions containing the depolarizer were placed in the porous cell; the acid (1:12) to act on the zinc

was placed in the outer vessel. The chromic acid was prepared by dissolving 1 lb. in 1 pint of water and adding 7 fluid oz. of H_2SO_4.

The relative values of the oxidants was brought out by plotting the results in curves. The potassium bichromate showed a rapid loss by polarization. The small amount of work possible with this salt justifies the statement that this once valued oxidant is worthless in batteries, compared with others now obtainable.

Bichromate of sodium and chromic acid are very nearly equal in merit, but the acid does rather more work. Both show an increasing current at first.

A solution in which chlorate of potassium is added to chromic acid shows an increased effect in the early part of the work.

The nitric acid curve, which extended over 30 hours before sinking to the level of the others, when the oxidant in all was exhausted, shows the vast superiority of this over all other oxidants, so far as the production of current is concerned.

The work in ampere-hours of each 400 grains was as follows: —

Nitric acid	16.0
Sodium bichromate	5.0
Potassium bichromate	1.7
Chromic acid	6.4

In this comparative test the nitric acid did not fall to the level of the rest, while the potassium bichromate has too much credit, as the last six hours of its curve belong to the zinc and acid alone.

96. Manganese Dioxide in Leclanché Cells. — The following contribution has recently been made by Mr. Eugene Obach[1] to the question, To what extent does the manganese dioxide furnish oxygen as a depolarizing agent in cells of the Leclanché type?

Representative samples were taken from two different brands of manganese peroxide and analyzed. No. 1 was found to contain 16.09 per cent of available oxygen, and No. 2, 15.55 per cent. Three medium Leclanché cells of ordinary construction were filled with each of the two brands of the dioxide, mixed with a suitable quantity of crushed retort carbon. The cells were then charged with the usual ammonium chloride solution, and each was closed through a resistance of 100 ohms, and the E.M.F. and internal resistance were measured from time to time. The tests showed that the three cells of each set were practically alike, and that there was scarcely any difference between the two brands of manganese.

For the first eight days the E.M.F. fell quite rapidly, but after that much more slowly. After the lapse of sixty-three days, when it had fallen to about one volt, the circuit was interrupted, and the cells were allowed to recover for a month. During this rest the E.M.F. recovered fully 25 per cent, but rapidly fell to its former value when the circuit was again closed, and then continued to fall at the same rate as before the interruption.

The experiment lasted 104 days, when the E.M.F. had fallen to half its initial value. One cell of each set was then selected, and the contents of the porous pot were weighed and examined. From the data thus

[1] London Electrical Review, May 15, 1891.

obtained, the weight of oxygen lost by the manganese dioxide could be determined. Since the total electrical output of the cell was known, the amount of oxygen required to dispose of all the displaced hydrogen could also be calculated.

The analysis of the manganese from the spent cells gave 14.83 per cent of available oxygen for No. 1, and 13.18 per cent for No. 2. From the total weight of the oxide of manganese present in each cell it was found that No. 1 had lost 4.57 grammes of oxygen, and No. 2, 3.87 grammes. The oxygen required by the electrical output, on the other hand, was 7.98 and 8.02 grammes respectively. It thus appears that the manganese peroxide furnished not more than half the oxygen to effect complete depolarization.

Two explanations are possible, with a probability that both of them are to some extent correct. It can hardly be doubted that an additional source of oxygen is the gas occluded in the carbon, and dissolved in the surrounding liquid. With ready access of air, and with frequent intervals of rest, it is possible that nearly enough oxygen may be supplied by the air to meet the requirements of the cell.

It is also quite likely that when such cells are worked hard, a considerable portion of the hydrogen evolved escapes with the ammonia in the gaseous form. This must occur in carbon cells without a depolarizer, and probably does so when the depolarizer is an insoluble solid, as in the instance described.

CHAPTER X.

GROUPING OF CELLS.

97. Activity and Efficiency. — Before deciding upon the best grouping of a given number of cells to accomplish a definite result, it is necessary to consider whether this result is to be attained with maximum activity or with maximum economy. The conditions of working will be different according as the one or the other is to be kept prominently in view.

Maximum activity involves the most rapid conversion of the energy applied into the energy of an electric current; maximum economy requires conditions so arranged that the work may be performed with the least loss; or, in other words, that the ratio of the work done to the energy expended shall be as large as possible. Maximum activity means that the work shall be performed with the greatest celerity; maximum efficiency means that it shall be done with the greatest economy. In the one case energy is sacrificed to time; in the other, time is sacrificed to economy.

98. Application of Ohm's Law to a Single Cell. — Let E be the E.M.F. of the cell, r the internal resistance, and R the external. Then, by Ohm's law, the current from a single cell will be

$$C = \frac{E}{R + r}.$$

If r is negligible in comparison with R, the current equals approximately $\frac{E}{R}$. The current is inversely as

the external resistance. In any case, whatever the value of r, the greatest current that a single cell can yield flows through it when the external resistance is zero. The current then equals $\frac{E}{r}$. But this condition involves the expenditure of all the energy in heating the cell. To obtain the greatest proportion of energy in the working circuit, the internal resistance should be made as small as possible. How large an internal resistance will be consistent with good economy depends upon the external resistance employed. Thus, with an external resistance of 4.5 ohms and an internal of 0.5, the loss internally is 10 per cent of the whole.

99. Cells in Series. — A battery of n similar cells may be grouped in several ways. When connected in series, the positive terminal of one cell is joined to the negative of the next, and its negative to the positive of the preceding. Thus the zinc and carbon, or metal composing the negative plate, of two adjacent cells are in metallic connection, the negative terminal of the first cell in the series, and the positive of the last being the only disconnected ones. These, therefore, constitute the terminals of the battery thus grouped in series, and the external circuit extends through the conductor from the one main terminal to the other.

So arranged, the total E.M.F. of the battery is the sum of the E.M.F.'s of the several similar cells, or nE; and the entire internal resistance is n times that of a single cell, since the current must pass in succession through the several cells. Hence

$$C = \frac{nE}{nr + R}.$$

If now the external resistance is small compared with

the internal, then R is negligible in comparison with nr, and

$$C = \frac{nE}{nr} = \frac{E}{r}, \text{ nearly.}$$

Under such conditions, an infinite number of cells in series cannot maintain a larger current than a single cell on short circuit.

If, however, r is negligible in comparison with R, then increasing the number of cells increases the current in nearly the same ratio. For then

$$C = \frac{nE}{R} = n\frac{E}{R}, \text{ nearly.}$$

100. Grouping in Parallel or Multiple Arc. — The only effect of such a grouping is to reduce the resulting internal resistance to $^1/_n$th that of a single cell. The positive terminals are all joined together, and the negatives likewise. These multiple terminals then constitute the main ones of the battery. All the cells side by side contribute equal shares to the output of the battery. The effect is precisely the same as if the n cells were replaced by one larger cell, with plates n times the area of those in the smaller cells. The cross-section of the liquid conductor is increased n-fold, and the internal resistance is reduced in the same proportion. Hence

$$C = \frac{E}{\frac{r}{n} + R}$$

The E.M.F. is in no way greater than that of one cell. But if now R is negligible in comparison with r, or even with $\frac{r}{n}$, then

$$C = \frac{E}{\frac{r}{n}} = n\frac{E}{R},$$

or the current is n times greater than can be obtained from a single cell.

101. Grouping in Multiple-Series. — A battery of n cells may be arranged in m series with l cells in each series. Then $n = ml$. The positive terminals of the several series are then coupled together; likewise the negative terminals. In this case the E.M.F. is increased to l times that of a single cell, and the resistance of each series is increased in the same proportion; but there are m parallel rows of cells, or m paths traversed by the current through the battery. The internal resistance is for this reason reduced to $^1/_m$th that of a single series. Hence

$$C = \frac{lE}{\frac{lr}{m} + R} = \frac{E}{\frac{r}{m} + \frac{R}{l}}.$$

102. Arrangement to Produce the Greatest Current. — From the last formula it is evident that the current will be the greatest when the denominator of the fraction is the least. If we multiply together the two terms of the denominator, $\frac{r}{m} + \frac{R}{l}$, the product, $\frac{rR}{ml}$, is a constant; for on the assumption that the resistance of each cell and the external resistance remain the same, their product, rR, is a constant; and the denominator ml is equal to n, the number of cells in the battery. Hence the product above is a constant. But when the product of two factors is a constant, their sum is least when they are equal to each other. Hence the sum of $\frac{r}{m}$ and $\frac{R}{l}$ is least when $\frac{r}{m} = \frac{R}{l}$, or when $\frac{lr}{m} = R$. This is therefore the condition for the greatest current of

constant value. But $\frac{lr}{m}$ is the internal resistance of the battery in multiple series, and R is the external resistance. Hence the internal should equal the external resistance for a steady current of maximum value.

This is also the condition for maximum activity for a fixed resistance R. The efficiency may be said to be 50 per cent, since half the energy is wasted internally and half externally, if none is stored up by electrolysis or by a motor mechanism.

103. Grouping of a Battery for Quickest Action. — In the preceding topics it has been assumed that the battery is to work with a steady current; and it has been found that to obtain the greatest current from a given number of cells, with a constant external resistance, the battery should be so grouped that the internal resistance shall be as nearly as possible equal to the external. But this is no longer true if the circuit contains an electro-magnet which is to be worked rapidly; such, for instance, as a vibrating bell or a Wheatstone's automatic transmitter. Such a circuit is said to possess the property of self-induction. Any change in the current flowing through it, either of increase or decrease, invokes an electromotive force of self-induction, which is always so directed as to oppose the change going on. When the circuit is closed, the E.M.F. of self-induction is opposed to that of the applied E.M.F., and its effect is to increase the time required for the current to grow to its maximum steady value. On opening a circuit, the self-induction prolongs the flow of the current, and manifests itself by the bright spark at the break. To take into account this property of a circuit, a term must be introduced into the expression for a current, additional to

those required by Ohm's law. This term depends for its value, at any instant after closing the circuit, upon what is called the coefficient of self-induction, denoted by L. The E.M.F. of self-induction is the product of this coefficient and the time rate of change of the current. Expressed in symbols the current then is

$$C_t = \frac{E}{R}(1 - e^{-\frac{R}{L}t}).$$

Here C_t is the value of the current at the time t after closing the circuit, R is the entire resistance, and e is the base of the Napierian system of logarithms, 2.7183. This is known as Helmholtz's equation.

If this equation is examined, it will be apparent that, at the time t, the value of the current falls short of its maximum by a factor depending upon the second term in the parenthesis. Whenever this factor becomes zero, the current will have the value assigned to it by Ohm's law. The effect of the self-induction in delaying the arrival of the current at its maximum value is expressed by this negative exponential term. The ratio $^L/_R$ is called the **time-constant** of the circuit. It is the time required for the current to rise to 0.632 of its final value. This time will be longer, the larger the value of L; or, conversely, the larger L is the smaller will be the current at any time t after closing the circuit.

The decimal fraction 0.632 is obtained in the following manner. If in Helmholtz's equation t be made equal to the time-constant $^L/_R$, then

$$1 - e^{-\frac{R}{L}t} = 1 - e^{-1} = \frac{e-1}{e}.$$

Substitute for e its value 2.7183, and we obtain 0.632. Therefore

$$C = \frac{E}{R} \times 0.632,$$

or during an interval equal to the time-constant of the circuit, the current will rise to 0.632 of its final value. If, for example, L is 5 units and R 10 ohms, the time-constant is one-half a second. In half a second the current then rises to 0.632 of its maximum value. This retardation in the growth of the current is due to the presence of coils and magnets in the circuit; the current is retarded because it has to create magnetic fields. Energy is stored up in these fields, and the resistance to the work done on them is manifested as an opposing electromotive force. As this opposition dies away, the effective electromotive force increases, and the current rises to its final value.

If now the current is to be worked with rapid interruptions, then it is desirable to reduce the time-constant to as small dimensions as possible. With a given coefficient of induction, the time-constant is inversely as the resistance. Hence this suggests the arrangement of the cells in series; for, while this arrangement diminishes the final value of the current, it also diminishes the time required for the current to rise to about two-thirds of this value; and it may easily follow that, for rapid working, the series arrangement will give a larger current in the short time during which the circuit remains closed, than could be obtained by the rule for grouping to get the greatest steady current.

An example will make this clear. Suppose twenty-four Daniell cells are available, each of 3 ohms resistance and 1 volt E.M.F. Let the external resistance be 5 ohms and the self-induction, L, 5 units (often now called henrys). Grouped in series, the total resistance of the circuit would be 77 ohms; in parallel, 5.125 ohms; and in four series of six cells each, 9.5 ohms. This last

arrangement is the one indicated by the rule for maximum steady current. The current in the three cases would have the final values 0.31, 0.195, and 0.63 of an ampere respectively.

Let us now compute the time-constant of the circuit in the three groupings. In the first it would be 5 divided by 77, or 0.065 sec.; grouped in parallel, 0.975 sec.; grouped for maximum current, 0.526 sec. In these times the current would rise to 0.2, 0.12, and 0.4 of an ampere for the three cases respectively. If now the circuit were interrupted as often as every tenth of a second, the current with the cells in series would rise in this time to something over 0.2 ampere; while the best grouping for steady current would, in the same time, give a current of only 0.109 ampere.

The current reaches 0.632 of its final value after an interval in seconds equal numerically to the time-constant of the circuit. At this instant the effect of the self-induction is the same as if the entire resistance in circuit had been increased 60 per cent. Hence the effect of self-induction is often likened to a spurious resistance.

104. Coupling Together Dissimilar Cells. — It is permissible to couple a battery in parallel or in multiple series only when all the cells are of the same type. Cells not differing much in E.M.F. or internal resistance may always be joined in series without detriment to any of them. If, however, the internal resistance of a cell is so large in comparison with the current flowing through the circuit in which it is placed that the fall of potential in passing through it is greater than the E.M.F. of the cell itself, then the addition of such a cell in series diminishes the effective voltage of the circuit, and so really diminishes the current.

If, for example, the resistance of the cell interposed in a circuit should be two ohms, and its E.M.F. one volt, then with one ampere current flowing through the circuit, the loss of potential in passing through the resistance of the cell would be two volts by Ohm's law, while the E.M.F. added would be only one volt. Such a cell contributes nothing to the production of a current. If its internal resistance were one ohm, under the conditions assumed, it would still contribute nothing to the current, but its own E.M.F. would simply make up for the loss due to its internal resistance. This can never occur with cells of the same type and size, unless the battery is on short circuit.

When dissimilar cells are joined in parallel by connecting together poles of the same sign, a short circuit is always formed of every pair of adjacent cells or adjacent parallel series. If now the E.M.F. of the one cell or series is not exactly equal to that of the adjacent parallel cell or series, then there will be an effective E.M.F. equal to the difference of the two, which will produce a current through the closed series of cells, discharging the one, and charging the other as if it were a storage battery. Thus, when the main circuit is open, some of the cells may be running down, even when the battery joined in multiple series or in parallel consists of similar cells; for some difference of E.M.F. always exists among commercial cells of the same type.

CHAPTER XI.

THERMAL RELATIONS.

105. General Considerations. — It has already b pointed out in Chapter I. that a battery is a device the conversion of the potential energy of chem separation into the energy of an electric current. wish now to consider more specifically the relati subsisting between the thermal energy of the chem changes taking place in a battery on the one hand, the current, electromotive force, and external work the circuit, on the other.

The basis of all such calculations is necessarily principle of the conservation of energy. This princi is stated by Maxwell as follows:[1] —

"The total energy of any material system is quantity which can neither be increased nor diminis by any action between the parts of the system, thou it may be transformed into any of the forms of wh energy is susceptible."

This principle has been experimentally verified cases where the energy of the systems investigated ta the form of heat, electricity, magnetism, etc. It is " one generalized statement which is found to be consist with fact, not in one physical science only, but in all

To this statement of the law of conservation energy should be added that of the dissipation

[1] Matter and Motion, Art. 74.

degradation of energy, viz. that all energy tends toward the form of uniformly diffused heat. And since, by the second law of thermo-dynamics, heat can be made to do work only by the transfer of heat from a hotter body to a colder one, uniformly diffused heat is energy in the unavailable form. Hence the available energy of any physical system, which Professor Tait calls Entropy, tends toward zero.

In any isolated system, such as a voltaic battery, with its electric circuit and translating devices included therein, energy is converted from one form into one or more others, but without loss or gain of energy. The proportion available for any useful purpose, however, becomes progressively less. If the circuit, external to the battery itself, is a simple non-inductive metallic resistance, then the transformed energy which appears first in the intermediate form of the energy of an electric current is all finally expended in heating the circuit. But if it contains an electrolytic cell, then a part of the energy undergoing change of form is stored up potentially in the chemical separation of electrolysis. If the current actuates an electro-motor mechanism, a part of the energy is transformed into mechanical work; and if electro-magnets or coils are included in the circuit, some of the energy is stored up in the magnetic field created by these coils and magnets. This portion of the transformation is a reversible one, and the energy is restored to the circuit when the applied E.M.F. is withdrawn. During the time that the current is rising to its final value, work is done against the E.M.F. of self-induction, and potential energy is accumulated in the magnetic strain produced by extending the lines of force about the circuit; while the current is falling

again to a zero value, the energy is restored to the circuit to assume the final form of heat.

In any cell the available energy is proportional to the mass of zinc or other metal composing the positive plate. But the same mass of zinc does not produce the same amount of electrical energy in cells of different types, because the chemical processes going on are different in different cells. In every case, however, the total energy at our disposal in a cell is dependent upon the chemical changes taking place; and these are the sole source of the energy, save in the exceptional cases in which energy is supplied by light or heat.

106. Units of Force, Work, Activity, and Heat. — In the system of units now almost exclusively used in science, the centimetre, the gramme, and the second are the three fundamental units in terms of which all other units are defined as derived units. Hence this is called the C.G.S. or centimetre-gramme-second system.

1. The unit of force is the **dyne**. It is that force which will give to a mass of one gramme in one second a velocity of one centimetre per second. Gravity is equal, therefore, to about 980 dynes.

2. The unit of work is the **erg**. It is the work done by a dyne in producing a displacement of one centimetre in the direction of the force.

3. The unit of activity, or rate of doing work, commonly called power, is the **watt**. It is the rate of doing work equal to 10^7 ergs per second. In engineering practice the **horse-power** is commonly used as the unit of activity when work is done on a large scale. It is equal to 33,000 foot-pounds per minute, or 550 foot-pounds per second. Reduced to the C.G.S. system, one horse-power is equivalent to 746×10^7 ergs per second, or 746 watts.

4. The unit of heat is the **calorie**. It is the heat required to raise one gramme of water from 0° C. to 1° C. The calorie is connected with the C.G.S. system by measuring experimentally the mechanical equivalent of one heat unit. This determination is rendered necessary by the fact that the Centigrade scale is independent of the C.G.S. fundamental units.

The result of the laborious experiments of Joule is that

$$1 \text{ calorie} = 4.2 \times 10^7 \text{ ergs (nearly)}.$$

More exactly, the heat required to raise a gramme of water through one Centigrade degree, if applied mechanically, will do 41,595,000 ergs of work.

107. The Heat Equivalent of a Current. — Since the difference of electrical potential between two points of a circuit is the work required to carry a unit quantity of electricity from one point to the other, there being no source of electromotive force between them, it follows that when Q units are transferred, the work equals

$$W = Q(V - V'),$$

where V and V' are the potentials at the two points.

But $W = HJ$, where H is the number of heat units; J is Joule's equivalent or 4.2×10^7; and $Q = C$, the current, if the time taken is one second.

Also the difference of potential between two points, under the above conditions, is equal to the E.M.F. required to produce the given current from one point to the other. Therefore $V - V' = E$.

Substituting these values, we obtain

$$HJ = CE = C^2R \text{ (by Ohm's law)}.$$

Whence $$H = \frac{C^2R}{J} = \frac{C^2R}{4.2 \times 10^7}.$$

Both C and R are taken in C.G.S. or "absolute" units; but if C is measured in amperes, or 10^{-1} C.G.S. units, and R in ohms, or 10^9 C.G.S., then

$$H = \frac{C^2R \times 10^7}{4.2 \times 10^7} = C^2R \times 0.24.$$

Also when a current of C amperes flows between two points on a circuit having a potential difference of E volts, then electrical energy is converted into heat between these points at the rate of CE watts, or $CE \times 10^7$ ergs per second; and the number of calories generated per second is

$$H = C^2R \times 0.24 = CE \times 0.24.$$

It follows that one watt is approximately equivalent to 0.24 calorie per second.

The first of the above formulæ for the heat generated per second is true for any homogeneous circuit or homogeneous parts of a circuit: it expresses a relation known as Joule's law. The second formula is true only when E is such that $C = \frac{E}{R}$.

108. Heat Evolved in a Circuit with no Counter Electromotive Force. — When the circuit contains no source of E.M.F. other than that of the battery itself, then by Joule's law

$$H = C^2(R + r)0.24 = CE \times 0.24 \text{ calories per second.}$$

But the total activity in the circuit is

$$W = CE \text{ watts.}$$

In this case all the energy transformed runs down into the form of heat. In the circuit interior to the electrodes the heat is

$$H_i = C^2r \times 0.24 \text{ calories per second.}$$

In the external circuit it is

$$H_e = C^2R \times 0.24 \text{ calories per second.}$$

These conclusions were accurately verified by Favre by determining, first, the quantity of heat evolved by dissolving 33 gms. of zinc in sulphuric acid; and, second, by determining the heat evolved by the consumption of 33 gms. of zinc in a Smee cell closed with a homogeneous conductor. These operations were conducted by introducing the vessel containing the zinc and acid into a huge calorimeter, or instrument for measuring heat, and observing the heat evolved. The Smee cell was subsequently introduced into the same instrument. The first operation produced 18,682 calories; the second, 18,674, a quantity almost identical with that due to the solution of the zinc under the simple conditions not involving an electric circuit.

By a further experiment, Favre measured separately the heat evolved internally and externally as regards the cell, and found the two quantities to be proportional to the corresponding resistances.

If any difficulty is found in understanding why the heat evolved is proportional to the square of the current, and not to its first power, it may be useful to consider how the activity is affected by doubling the current while the resistance of the circuit remains the same.

If we imagine the E.M.F. doubled by doubling the number of cells in series, then the double current means that twice as much zinc is dissolved in each cell per second; and since the number of cells is doubled, the mass of zinc dissolved in the whole battery becomes four times as great as before. But the heat is also increased four-fold by doubling the current. The mass

of zinc dissolved is a measure of the activity in the circuit. The activity is quadrupled because its measure, the product of C and E, is quadrupled by doubling both C and E simultaneously.

109. Counter Electromotive Force in a Circuit. — The entire activity, or rate at which a battery is supplying energy, may be represented in part by the heat evolved in accordance with Joule's law, and in part by other work done, such as the chemical separations in electrolysis, the mechanical work of a motor, or in heating junctions of dissimilar substances by reason of the E.M.F. arising at such a junction, and known as the Peltier effect.

We may, therefore, write for the energy expended in the circuit in time t,

$$CEt = C^2Rt + AC.$$

The first term of the second member of this equation is the heat waste; and the second, the work done on the external agent. This second quantity is in every case proportional to the current, and A is the constant required to express the activity other than that spent in heating the circuit.

Dividing the equation through by Ct and transposing,

$$C = \frac{E - \frac{A}{t}}{R}.$$

R is here the entire resistance of the circuit. It is evident that the quantity $\frac{A}{t}$ is of the nature of an E.M.F. Moreover, it has the negative sign. It is therefore a back or counter E.M.F. The effective E.M.F. producing a current is the applied E.M.F. less the back

E.M.F. arising from the fact that work of some kind is done against a resistance. The only reaction that the agent can offer to the work done upon it under the electric pressure must be of the same nature as that of the applied activity, viz. an E.M.F. This counter E.M.F. is a necessary factor in every case in which work is done by electricity.

110. Division of the Energy in a Circuit with Counter Electromotive Force. — If E' represents the counter E.M.F., then the equation for the current becomes

$$C = \frac{E - E'}{R}.$$

But the heat waste in watts is, by Joule's law,

$$C^2R = C(E - E') = CE - CE'.$$

Now CE is the total activity of the battery furnishing the current. The heat generated in the entire circuit of resistance R is less than this by the quantity CE' watts. Hence the energy spent in doing work is the product of the current and the counter E.M.F. The ratio of the work done to the energy wasted in heat is

$$\frac{CE'}{C(E - E')} = \frac{E'}{E - E'}.$$

It is evident, therefore, that the relative activity concerned in the work done bears to the heat waste a larger ratio the larger E' becomes. But the larger E' is the smaller is the current. Maximum efficiency thus requires a small current or small activity. It can easily be shown that maximum activity involves an efficiency of 50 per cent.

111. Counter Electromotive Force of Electrolysis. — In the general equation of section 109, AC represents that

portion of the energy expended in the entire circuit which does not appear as heat in virtue of simple ohmic resistance. In electrolysis this energy is expended in the work of chemical decomposition, or in conferring potential energy upon the separated components or ions of a chemical compound. The process involves an increase in the intrinsic energy of the substance. Whenever the volume of the products of this decomposition is greater than that of the electrolyte, additional mechanical work is done in overcoming the pressure. If the electrolyte is a liquid, and the products are gases which fulfil Boyle's law, then for the same temperature the product of the volume and pressure is a constant. This product represents the mechanical work done. Hence the electromotive force required to effect the decomposition will be sensibly independent of the pressure of the liberated gas.

Let z represent the electrochemical equivalent of an ion, and h the heat of combination of a gramme of this ion with an equivalent mass of the other ion. The electrochemical equivalent is the quantity of the substance electrolyzed by the passage of unit quantity of electricity. Hence the quantity electrolyzed by current C in time t is Czt; and the energy expended is $CzthJ$. But this is also represented by CA. Therefore

$$zhJ = \frac{A}{t}.$$

Now $\frac{A}{t}$ has been found to be the value of the counter electromotive force E', and zhJ is the mechanical equivalent of the chemical action on one electrochemical equivalent of the ion. This may be made to include any mechanical work done in changing the molecular

aggregation against pressure. Therefore the counter electromotive force present in an electrolytic apparatus is equal to the mechanical equivalent of the chemical and mechanical actions involved in electrolyzing one equivalent of the substance. These conclusions have been verified by many experimenters.

112. Failure of a Cell to Effect Decomposition. — If the counter electromotive force of the electrolytic cell is greater than the direct electromotive force of the battery, then electrolysis cannot take place. For in this case $C = \frac{E - E'}{R}$ is negative, which means that the electrolytic cell would produce a current back through the battery. Moreover, since CE represents the energy expended per second by the battery, and CE' the activity necessary to do the work of electrolysis, it is evident that the counter electromotive force cannot grow to its maximum value, since the battery is deficient in the necessary activity. It is for this reason that the Smee cell cannot decompose water.

While these conclusions are correct as regards actual decomposition, it is nevertheless true that any electromotive force, however small, will produce a current through an electrolyte which obeys Ohm's law. Actual decomposition does not take place till the electromotive force reaches a finite magnitude determined by the considerations already explained.

The theory of Clausius respecting the continuous interchange of like atoms between different molecules of a liquid serves to explain the flow of a current without visible decomposition. Clausius supposes that the same individual atom is at one time associated with an atom of the opposite kind, and at another time with

another. In other words, decomposition and recomposition are continually going on in an electrolyte in an irregular way, when no current is flowing; but the application of an electromotive force serves to give this process a definite direction. If the electromotive force reaches a definite value for any given electrolyte, then the accumulation of the ions in finite quantity upon the electrodes gives rise to the counter electromotive force of polarization. According to this view, which is approved by Maxwell, the electromotive force of polarization depends upon the deposit of the products of the decomposition on the electrodes. But this deposit is constantly tending to become free, by diffusing through the liquid or escaping as a gas. If the decomposition is so slow that the separated ions may pair again with new partners, or disappear by diffusion, instead of accumulating at the electrodes, then no visible decomposition takes place. But a current of small magnitude still continues to flow in accordance with the law of Ohm. The density of the ions on the electrodes is so slight that only a feeble state of polarization is produced. The dissipation of the ions by diffusion or other means is then very small, and the strength of current is really limited by this small rate of dissipation.

113. Calculation of E.M.F. from the Heat of Combination. — It has been shown in section 111 that the counter electromotive force of an electrolytic cell equals zhJ, or the mechanical equivalent in ergs of the chemical energy due to one electrochemical equivalent of the substance electrolyzed. The same principles may be applied to the calculation of the E.M.F. of a battery; for it may be provisionally assumed that the total energy of the chemical reactions appears in the

intermediate form of the energy of an electric current before assuming other forms, provided no local action takes place which contributes nothing to the electric energy. The chemical processes going on in the cell involve a loss in the intrinsic energy of the materials. This loss represents the energy which takes the form represented by the electric current. If this loss can be calculated from thermal data, it may be placed equal to the activity of the electric circuit.

If we suppose that only two chemical changes take place, as in the Daniell cell, in which $ZnSO_4$ is formed and $CuSO_4$ is decomposed; and if z and z' are the electrochemical equivalents of the two electropositive ions, and h and h' their heats of formation for one gramme of each (in the combinations in which they appear in the battery); then, for a current C, the loss of chemical potential energy per second is

$$(Czh - Cz'h')J \text{ ergs.}$$

But the electrical energy developed is $CE \times 10^7$ ergs per second. Therefore, equating the two,

$$CE \times 10^7 = C(zh - z'h') 4.16 \times 10^7,$$

or

$$E = (zh - z'h') 4.16.$$

If Σ be used to represent "the sum of such terms as," then we may write

$$E = 4.16 \Sigma zh,$$

so as to include all the chemical actions involving thermal changes. This formula may be put into a more convenient form for use in connection with tables giving heats of combination.

The electrochemical equivalents are proportional to

the chemical equivalents of the substances; that is, to the relative weights of the substances which take part in chemical reactions. If, therefore, we know the electrochemical equivalent of hydrogen, the others may be found by multiplying by their chemical equivalents. The electrochemical equivalent of hydrogen in grammes per coulomb is 0.00001036. If now the heat of combination of one chemical equivalent of an ion is H, then 0.00001036 H equals zh. Consequently

$$E = 4.16 \times 0.00001036 \Sigma H,$$

or

$$E = 0.000043 \Sigma H.$$

It is only necessary then to find the algebraic sum of the heats of combination for a chemical equivalent of each ion taking part in the reaction in order to find the E.M.F. in volts. If, in the formula, E becomes unity, then the number of calories corresponding to one volt is the reciprocal of the constant 0.000043, or 23,200. In this discussion the chemical equivalents used are half atomic weights of bivalent substances, corresponding to one of hydrogen, which is univalent. With this condition one volt is equal to 23,200 calories. If the chemical equivalents used are the atomic weights of bivalent elements, and double those of the univalent ones, then a volt is numerically equal to 46,400 calories.

114. Application to the Smee Cell. — The chemical action consists in the formation of zinc sulphate at the expense of hydric sulphate or sulphuric acid.

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

Heat of formation of Zn, O_2, SO_2 . 79,495 calories.
" " H_2, O_2, SO_2 . 60,920 "
$\therefore \Sigma H = 18,575$ "

Therefore $E = 0.000043 \times 18,575 = 0.80$ volt.

These thermal values are from Thomsen's determinations. Since $ZnSO_4$ is formed, and H_2SO_4 is decomposed, the resulting heat of combination is the difference between the thermal values of the two similar operations.

According to the determinations of Berthelot the heats of formation are as follows: —

Heat of formation of	Zn, S, O_4 . .	121,000 calories.
" "	H_2, S, O_4, . .	100,500 "
	$\therefore \Sigma H =$	20,500 "

Therefore $E = 0.000043 \times 20{,}500 = 0.88$ volt.

115. Application to the Daniell Cell. —

Reaction, $Zn + ZnSO_4 + CuSO_4 = 2\,ZnSO_4 + Cu$.

One molecule of $ZnSO_4$ is formed every time one molecule of $CuSO_4$ is decomposed. After Thomsen we have —

Heat of formation of	Zn, O_2, SO_2 .	79,495 calories.
" "	Cu, O_2, SO_2 .	55,745 "
	$\therefore \Sigma H =$	23,750 "

Therefore $E = 0.000043 \times 23{,}750 = 1.02$ volts.

After Berthelot we have —

Heat of formation of	Zn, S, O_4 . .	121,000 calories.
" "	Cu, S, O_4 . .	95,700 "
	$\Sigma H =$	25,300 "

Therefore $E = 0.000043 \times 25{,}300 = 1.087$ volts.

116. Application to the Bunsen Cell. —

Reaction, $Zn + H_2SO_4 + 2\,HNO_3 = ZnSO_4 + 2\,H_2O + 2\,NO_2$.

We have then to find the heat of combination of zinc sulphate, water, and peroxide of nitrogen; and from

their sum subtract the heat of formation of the decomposed sulphuric and nitric acids.

After Thomsen we have —

Heat of formation of	Zn, O_2, SO_4 .	79,495 calories.
" "	$2(H_2, O)$ . .	68,360 "
" "	$2(NO, O)$ . .	19,570 "
Total		167,425 "
Heat of formation of	H_2, O_2, SO_2 . .	60,920 calories.
" "	$2(H, NO, O_2)$.	63,185 "
Total		124,105 "

Therefore $\Sigma H = 167,425 - 124,105 = 43,320$;

and $E = 0.000043 \times 43,320 = 1.863$ volts.

117. Application to the Silver Chloride Cell. — If we assume the cell set up with a dilute solution of zinc sulphate, then the result of the action taking place when the cell is in operation is the formation of zinc chloride and the decomposition of silver chloride. Hence we have only to find the difference between the heats of formation of the two chlorides.

From Thomsen's investigations these are —

Heat of formation of	Zn, Cl_2 . . .	56,420 calories.
" "	Ag_2, Cl_2 . . .	29,380 "
	$\therefore \Sigma H =$	27,040 "

Therefore $E = 0.000043 \times 27,040 = 1.16$ volts.

118. Helmholtz's Formula for Electromotive Force. — The direct measurement of the E.M.F. of a battery rarely gives a result agreeing exactly with the value calculated from the thermo-chemical data of the reaction accompanying the work of the battery. Helmholtz has

accordingly modified the formula from thermo-dynamic considerations so as to express the E.M.F. by the equation,

$$E = 0.000043\,C \pm T\frac{dE}{dT},$$

in which C equals the heat of the reactions, E the electromotive force, and T absolute temperature, or temperature reckoned from a zero equal to − 273 of the Centigrade scale. The last term of the equation expresses a general relation which may admit of different interpretations. We may suppose that the chemical energy can be only partially transformed into electric energy, while the rest is directly converted into heat. Or an explanation of the discrepancy may be sought for in phenomena that tend to prevent the integral transformation of the chemical energy.

An examination of this problem has been undertaken by Chronstchoff and Sitnikoff.[1] They have applied to the solution of the problem the thermo-electromotive force produced by the passage of a current at the contact surfaces of liquids and metals in a battery. This is known as the Peltier phenomenon. The expression for this E.M.F. of thermal origin is identical with the final term of the Helmholtz equation, which represents the difference between the chemical heat and the voltaic heat of a battery; and the question arises whether they are equivalent expressions for the same identical quantity.

The results of their experimental investigation of the problem raise a strong probability at least that this explanation is the correct one. One or two examples must suffice to illustrate the application of this method

[1] Comptes Rendus, Tom. 108, 1889.

to the explanation of the discrepancy existing between the observed value of the E.M.F. and that calculated from thermo-chemical data.

The thermo-electromotive forces of the metal-liquid contacts were carefully measured by the experimenters in each case.

1. Case in which the E.M.F. observed is greater than the calculated value.

$$\mathrm{Pb} \mid \mathrm{PbSO_4} \mid \mathrm{ZnSO_4} \mid \mathrm{CuSO_4} \mid \mathrm{Cu}.$$

$$E = 0.61 \text{ volts at } 20^\circ \text{ C.}$$

E calculated from thermal values of $CuSO_4$ and $PbSO_4$ is 0.383.

The thermo-electromotive force for the system

$$\mathrm{Cu} \mid \mathrm{CuSO_4} \mid \mathrm{Cu},$$

between 0° to 50°, was found to be $0.00066 = \frac{dE}{dT}$.

For the system

$$\mathrm{Pb} \mid \mathrm{PbSO_4} \mid \mathrm{ZnSO_4} \mid \mathrm{PbSO_4} \mid \mathrm{Pb},$$

$$\frac{dE}{dT} = -0.00011 \text{ volt.}$$

The value of $T\frac{dE}{dT}$ is therefore $293 \times 0.00077 = 0.225$ volt.

Then $0.383 + 0.225 = 0.608$ volt.

This is almost exactly identical with the observed value.

2. Case in which the observed E.M.F. is less than the calculated value.

$$\mathrm{Zn} \mid \mathrm{ZnSO_4} \mid \mathrm{PbSO_4} \mid \mathrm{Pb}.$$

$$E = 0.500 \text{ volt at } 20^\circ \text{ C.}$$

E calculated from thermo-chemical data of $ZnSO_4$ and $PbSO_4$ is 0.697 volt.

The thermo-electromotive force for the system

$$Zn \mid ZnSO_4 \mid Zn$$

was found to be 0.00076 volt per degree.

For the system

$$Pb \mid PbSO_4 \mid ZnSO_4 \mid PbSO_4 \mid Pb,$$

$$\frac{dE}{dT} = -0.00011 \text{ volt as before.}$$

Hence $T\frac{dE}{dT} = 293 \times 0.00065 = 0.190$ volt,

and $E = 0.697 - 0.190 = 0.507$ volt.

In this last example the authors of the paper appear to have made an error in respect to the sign of $\frac{dE}{dT}$ for $Pb - PbSO_4$. The corrected value gives $E = 0.473$ volt.

The conclusion derived from all the experiments is that the Peltier effect is of a nature to make up for the discrepancy between the electromotive force observed directly, and that calculated from the thermal values of the chemical actions. The Peltier effect gives a value of the same sign and of the same order as this difference.

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